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VOLUME XVI, PART 2

1924

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TRANSACTIONS OF THE AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

NOTES ON THE DEVELOPMENT OF THE DU PONT CYANIDE PROCESS

By H. G. CHICKERING

Read before the Pittsburgh Meeting, December 6, 1924

From the commercial standpoint, cyanogen probably reached its peak of importance just prior to and during the World War, owing to its value as a nitrogen-bearing compound, and the eyes of many anxious investigators were turned toward the cyanides and cyanamides during those years for a means of fixing our nitrogen requirements. It was such a motive which prompted the du Pont company in 1918 to investigate intensively the subject of sodium cyanide from a nitrogen-fixation standpoint, for the production of ammonia and nitric acid, both of which are used to a great extent in the manufacture of explosives. While it was realized that during normal times any cyanide process would probably be unable to compete with other synthetic processes for the production of ammonia, the importance of a method for the manufacture of a high-grade cyanide and the many important chemical compounds which may be produced from such a raw material was recognized.

A literature and patent search resulted in a decision to investigate the production of sodium cyanide in a manner represented by the following equation:

$$Na_2CO_3 + 4C + N_2 = 2NaCN + 3CO.$$

Briefly stated, the du Pont process for making cyanide consists in heating a mixture of soda ash, carbon and catalyzers to approximately 975 deg. C. in gas-fired retorts with nitrogen passing through the mass under a pressure of 15 lb. to the sq. in. gage. The product from the retorts is leached with water to form a saturated cyanide solution, from which sodium cyanide is crystallized in pure form, the undissolved residue containing the catalyzers being used to make up the next furnace charge and the mother liquor from the crystallizing operation being used for further leaching. The cyanide crystals are dehydrated in evaporators and in hydraulic presses, which discharge anhydrous cyanide in cakes of convenient form.

Experimental Development

In our earlier experimental work emphasis was laid on a study of the influence of various catalyzers on the rate and manner of nitrogen fixation, a determination of the proper proportions of the

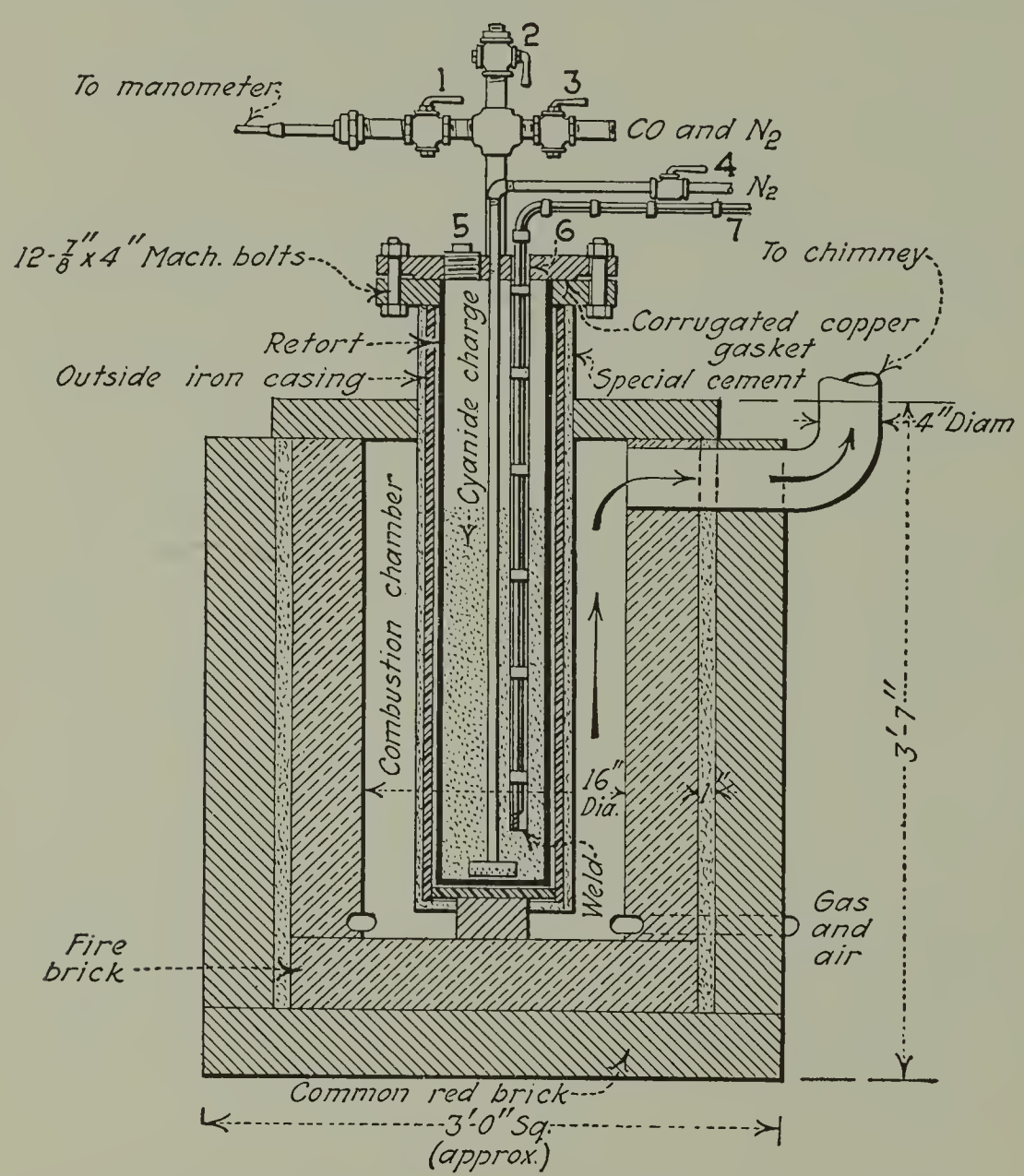


Fig. 1. Small Experimental Retort Used in Early Experiments

It consists of an iron retort capable of withstanding a pressure of 15 lb. per sq. in. gage, at temperatures ranging from 900 to 1,100 deg. C. It has a flanged head provided with means for introducing nitrogen, as at 4, ending in a distributor shown at the lower portion of the retort; a charging hole with plug 5, for introducing the charge; and an outlet pipe for the escape of the gases given off in the reaction, this pipe being so arranged as to accommodate a manometer and a valve for sampling. The retort was fitted with the usual pyrometer pocket 6, and thermocouple 7, for controlling the temperature of the operation. The retort proper was set within an outside iron casing, which was covered with fireclay cement to protect it from oxidation by the gases of the combustion chamber. The capacity of this experimental unit was about 30 lb. of charged material.

three ingredients that constitute a retort charge, and a study of the optimum conditions of temperature and pressure in the retort. The experimental retort is shown in Fig. 1.

Up to this time ground metallurgical coke had been used as a source of carbon with the addition of finely divided iron as a catalyst. A great many auxiliary catalysts were used along with the iron, of which alkali halides were found to be the best. It was ultimately found that the use of iron oxide together with an alkali halide—such, for instance, as sodium fluoride—mixed with soda ash and ground coke, increased the conversion from about 50–55 per cent to about 70 per cent in four-sevenths of the original time. The results of this small scale experimental work are shown in Table I, from which it will be noted that when no catalyzer is used a 45 per cent conversion was obtained in 7 hours as compared with a conversion of 70 per cent in 4 hours, when a catalyzer consisting of ferric oxide and sodium fluoride was used. The charges used at this time consisted of approximately 40 per cent C., 40 per cent Na_2CO_3, 15 per cent Fe_2O_3 and 5 per cent NaF, first powdered finely and afterward thoroughly mixed.

In this process the question of retort pressures is important and it was definitely shown by a series of experiments that 15 lb. per sq. in. gage pressure represented the optimum pressure conditions—that is to say, that a pressure of 15 lb. per sq. in. gave an effect as good as pressures up to 50 lb. and a better effect than pressures of a lower degree.

It was next determined that pure nitrogen was entirely unnecessary in this process. With producer gas as the source of nitrogen, substantially the same amount of cyanide is formed in a given time and at the usual temperature, provided two important precautions are observed:

(*a*) The producer gas must have a minimum CO_2 content (not more than 6 per cent by volume), and

(*b*) Any cooling down of the cyanized charge in the presence of producer gas must be avoided.

Carbon dioxide destroys cyanide rapidly even at high temperatures, and consequently the producer gas used must contain a minimum amount of this impurity. Likewise, the cyanized charges cannot be cooled in an atmosphere of producer gas, because, although the equilibrium $2CO \longleftrightarrow C + CO_2$ gives almost pure CO above 900 deg. C., at 500 to 600 deg. C. it is almost completely reversed.

The use of metallurgical coke in this process has its disadvantages, which are principally due to its high ash-content and low activity. Several other forms of carbon were investigated with a view to obtaining a source of pure active carbon that would not be prohibitive as regards cost. The search led ultimately to the finding of such a material in the carbon produced as a little used byproduct in the preparation of wood pulp for the manufacture of paper by the soda process.[1]

This material is represented by the following typical analysis:

	Per Cent		Per Cent
Soda ash	2.5	Volatile matter	30
Water insoluble ash	2.5	Fixed carbon	65

This byproduct carbon when substituted for metallurgical coke in charges otherwise of the same composition and furnaced under the same conditions gave:

(*a*) A substantial increase in the conversion of soda ash to cyanide.

(*b*) An average of from 40 to 45 per cent cyanide in the furnace product as against a previous average of 35 per cent.

(*c*) A shortening of the time required for the economically complete cyanide reaction of from 4 hours to 2 hours, when oxide of iron and an alkali halide were used as catalyzers.

The only disadvantage encountered with the use of this form of carbon was due to its very finely divided state and its low density. It was found impossible to keep it from being blown from the powdered charge out of the retort when once the current of producer gas was admitted. It was, therefore, necessary to incorporate the charge in a wet mixer, adding sufficient water to hydrate the sodium carbonate present. The mass after being allowed to harden was granulated in a corning mill, the fines being screened out and returned to the wet mixer.

The next major chemical development pertained to the substitution of "black liquor" for commercial soda ash and the byproduct carbon just described. The black liquor used in all our

[1] In this process, wood chips are digested with caustic soda solution, and thus pulped. The exhausted caustic solution is separated from the pulp, and evaporated to form "black liquor," a concentrated caustic solution carrying partly carbonized wood particles and partly decomposed resinous compounds dissolved from the pulped wood. The soda pulp manufacturer recovers the soda from this black liquor by incineration and leaching. Soda ash solution and a pure, finely divided carbon byproduct are thus produced. The soda ash is causticized with lime for re-use in the pulping operation.

work, which was obtained direct from a paper pulp manufacturer, is the liquor resulting from the evaporation of the caustic soda solution with which the wood is cooked. It is a black, viscous liquid with a specific gravity of about 35 deg. Bé. and contains excess caustic soda from the digestion of wood chips to dissolve ligneous and resinous matter, together with compounds resulting from the reaction between these constituents of wood and the surplus of caustic soda present. A typical analysis of black liquor as obtained from a pulp mill follows:

	Per Cent
Soda ash (potential)	23.0
Fixed carbon	13.5
Water and carbonaceous material, volatile at 250°C. (mostly water)	56.0
Carbonaceous material, volatile at 300 deg. C.	7.0
Ash	.5

Investigation showed that if, instead of incinerating the black liquor by the usual method, through which the black ash becomes heated to a high temperature, the black liquor be evaporated to dryness at low temperatures and the residue heated out of contact with air, practically complete thermal decomposition of the organic compounds takes place at temperatures between 250 and 350 deg. C. There resulted an extremely porous mass containing 60 to 65 per cent soda ash and 40 to 35 per cent carbon (a large part of the carbon being in colloidal condition), entirely suitable as a source of soda ash and largely fulfilling the carbon requirements for a cyanizing charge.

It was definitely demonstrated that charges prepared by using black liquor, augmented by the addition of byproduct carbon, would produce a product containing 50 to 55 per cent NaCN in 70 per cent of the furnacing time previously required. (See Table I.)

TABLE I

ILLUSTRATION OF IMPROVEMENT IN CONVERSION

Small Experimental Retorts Operated at 950°–1,000°C.

Charge	Conversion (Per Cent Theoretical)	Time Hours	Per Cent NaCN in Product
Soda ash and coking coal	45	7	—
Soda ash, coke and iron	55	6	25
Soda ash, coke, iron and alkali halides	70	4	35
As above with substitution of byproduct carbon for coke	75	2	40–45
As above with substitution of black liquor for soda ash and byproduct carbon	90	1½	50–55

The Step-Up to Commercial Units

By this time the process had reached a point in its development where it was deemed advisable to consider commercial-size units. One of our first decisions pertaining to plant-scale operation was to discard the "continuous feed" retort principle in favor of the "batch process" method. This decision was largely influenced by considerations of equipment cost, together with our knowledge

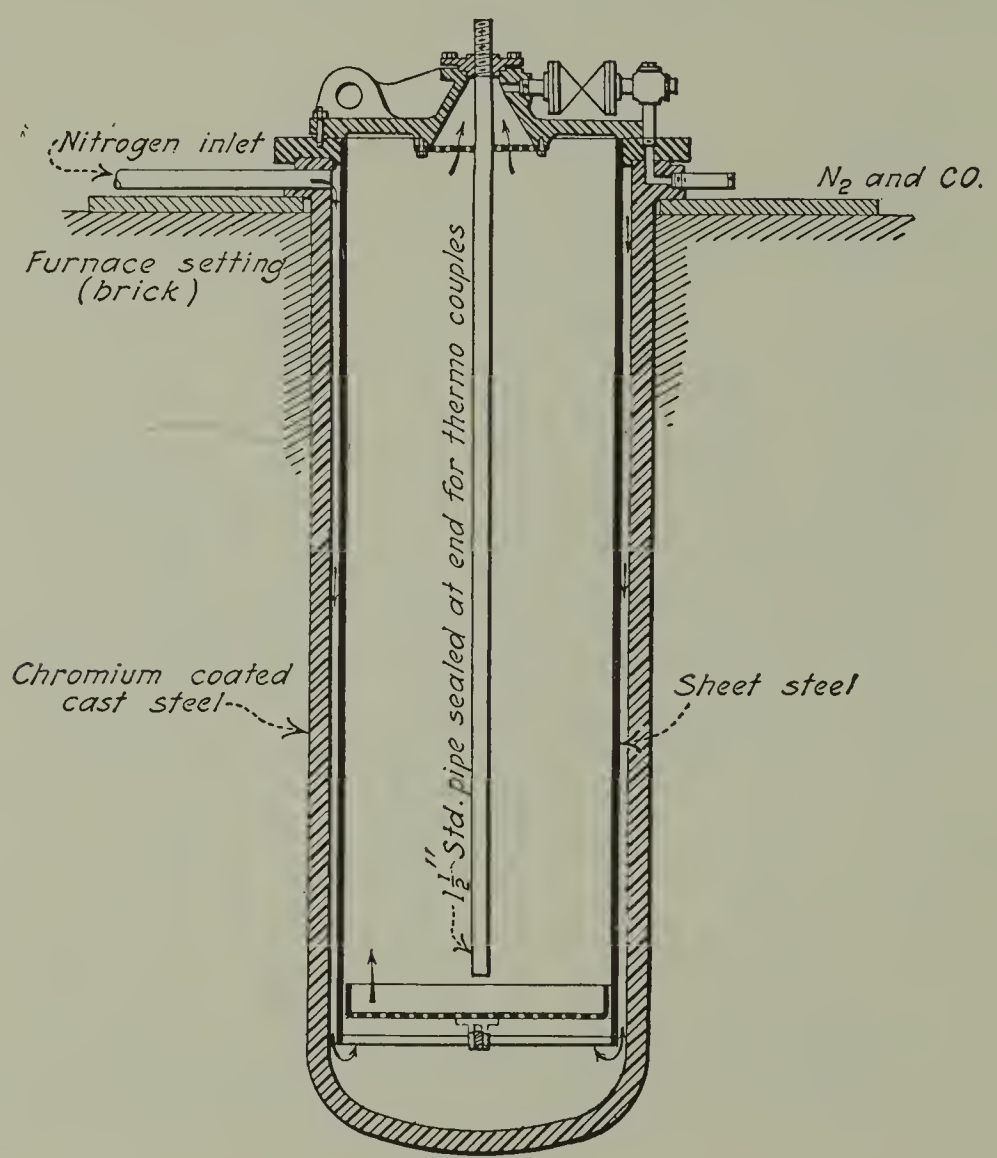


Fig. 2. Retort Finally Developed

from the past experience of others that very great difficulty would be faced in feeding semi-molten cyanide charges continuously through a heat zone raised to the temperature for cyanide reaction. Further, since it had been decided to use producer gas as our source of nitrogen, the fact that cyanide decomposition would result from cooling cyanide charges in producer gas made successful continuous-feed retort operation with producer gas seem very improbable.

Means devised for avoiding batch process disadvantages con-

sisted in inclosing the charge in a light, sheet-iron container inserted in the retort proper, the retort remaining permanently in the furnace setting, which could be maintained at constant temperature. The charge-container, with its contents, at the end of the reaction period could then be easily removed and cooled in a suitable cooling chamber and a new container holding a raw charge could be immediately inserted in the permanently fixed heavy retort.

The design of retort as finally developed is shown in Fig. 2, and the following advantages in operation are obtained:

(*a*) Batch charges can be furnaced on much the same time schedule as if the charges were fed through the retort continuously, the principal difference being the interval of time required for removing, by means of a crane, a finished charge and inserting another envelope containing a new charge.

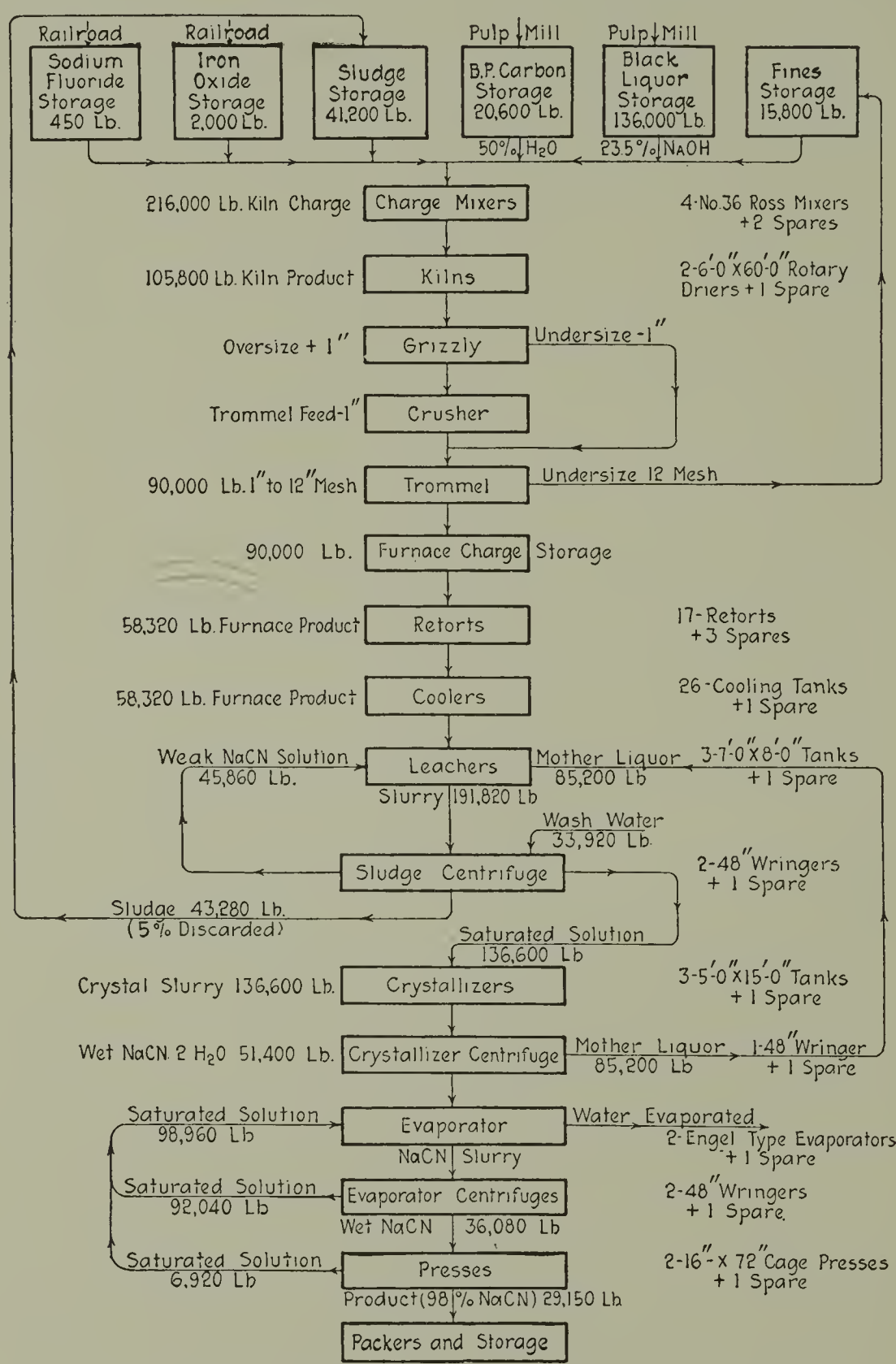
(*b*) The retorts proper are maintained constantly at the operating temperature, thus avoiding troubles due to their alternate heating and cooling.

(*c*) The nitrogen in its passage down from the top of the heated annular chamber formed between the inside walls of the retort and the envelope containing the charge becomes preheated to the reaction temperature when it reaches the perforations admitting it to the charge, thus heating the charge internally. This means of heating the charge tends to flatten out the temperature gradient between the walls and center of the retort charge.

A great deal of attention was given to the subject of retort protection, which eventually led to the development of an entirely new process for the production of heat and oxidation resistant castings, known as "chromium-coated castings." Such castings are made by coating the molds with ferrochrome in such a manner as to form a high chrome-iron alloy on the outside surface of the iron or steel castings when the metal is poured. The subject of chromium-coated castings, while of importance in connection with any process that involves furnace oxidation problems, is too extensive to receive more than brief mention here. Fortunately there are several very good oxidation-resisting materials on the market at this time which can be successfully used in this cyanide process.

Another important operating detail developed at this time resulted from observations of the physical condition of retort charges at different stages of the cyanide reaction. It was found that shrinkage in the volume of the charge began to take place soon after reaction started and that this shrinkage amounted to about one-half the original volume of the charge after the reaction was one-fourth completed. Therefore advantage was taken of this

phenomenon by adding more material to the retort at the end of this shrinkage period. In this simple manner 50 per cent additional product of the same cyanide content was obtained with the ex-



Flow Sheet of the Process

penditure of less than half an hour of added time, including that required for interruption of the operation and for introducing the augmenting charge.

It is a surprising fact, as disclosed by a literature search, that previous investigators had always used retorts of relatively small diameter. It has been shown conclusively that the rate of cyanide formation is directly proportional to the rate at which heat reaches the charge when once the charge has been brought up to temperature. Using vertical cylindrical retorts varying from 8 to 24 in. in diameter, it was further discovered that the heat is transmitted through the charge so largely and so rapidly by radiation that the rate of transmission depends principally upon the ratio of heat-transfer surface in the retort walls to the volume of the charge. The effect of this discovery is illustrated by the following comparison of cylindrical retorts of 8 and 24 in. diameter, respectively:
8 in. diam. retort:

$$\frac{25 \text{ in. circumference}}{50 \text{ sq. in. area}} = \frac{25 \text{ sq. in. heat-transfer surface}}{50 \text{ cu. in. charge}} = \frac{1}{2} = 0.5;$$

24 in. retort:

$$\frac{75 \text{ in. circumference}}{450 \text{ sq. in. area}}$$

or

$$\frac{75 \text{ sq. in. heat-transfer surface}}{450 \text{ cu. in. charge}} = \frac{1}{6} = 0.166.$$

The rate of heat transmission and consequently of cyanide formation in an 8 in. diameter retort is therefore roughly 0.5 as compared with 0.166 in a 24 in. diameter retort. This means that while a 24-in. retort will consume 0.5 ÷ 0.166, or three times as much time for reaction, approximately 450 ÷ 50, or nine times as much product can be handled. On the basis of such considerations, it was decided to employ retorts about 36 in. in diameter by 12 ft. long, set vertically.

The final and to a large extent the most noteworthy achievement in the chemical development of this process consisted in devising a method for extracting technically pure cyanide from the retort charges by aqueous leaching. That this was possible was evident from a thorough investigation of the mutual solubilities of sodium cyanide, sodium carbonate, sodium hydroxide and sodium fluoride. The data thus obtained showed the strongly depressing effect of the cyanide and hydroxide on the solubilities of the carbonate and fluoride, and resulted in the development of a method for recovering 96 per cent of the cyanide in the furnace product as a material of from 96 to 98 per cent purity. The success of this

method depends largely upon the maintenance of a definite small hydroxide concentration in the leach liquors. The method involves:

(*a*) Simple, countercurrent leaching to saturation at 35 to 40 deg. C., followed by crystallization at 8 to 12 deg. C., with the production of 98 + per cent pure $NaCN.2H_2O$.

(*b*) The use of mother liquor from the crystallizing operation in further leaching operations.

(*c*) The use of wash water in the leaching operation in amount only sufficient to replace the water removed by crystallization of the hydrated cyanide.

(*d*) The "melting" of the $NaCN.2H_2O$ crystals in their own water of crystallization in a "salting-out" evaporator, operating in closed circuit with a centrifuge which separates the anhydrous cyanide deposited in the evaporator from the saturated cyanide solution simultaneously formed, and returns this solution to the evaporator.

(*e*) The dehydration of the wet anhydrous cyanide under hydraulic pressure at 45 to 50 deg. C. with the production of cyanide cakes of 96 to 98 per cent purity.

(*f*) The return of the press liquor to the evaporator.

(*g*) The prevention of accumulation of the very soluble sodium hydroxide in the leach liquors by transforming it to carbonate through treatment with sodium bicarbonate.

The Present Process

This process in its present state of development differs considerably from the simple process first described in this article. We now find our raw materials consisting of soda pulp mill "black liquor" and "byproduct carbon" as the sources of soda ash and carbon, while producer gas is used as a source of nitrogen. The use of these materials, while constituting great advantages as regards conversions, yields, operating costs, etc., complicates the process somewhat so far as equipment and, therefore, investment costs are concerned. There is included in this paper a flow sheet of which detailed explanation does not appear necessary. It is perhaps sufficient briefly to enumerate the important steps of the process as now developed.

The retort charge, consisting of the raw materials mentioned above, together with sludge recovered from the leaching operation and "make-up" iron oxide and sodium fluoride, is fed into charge mixers, whence it flows by gravity to rotary driers fired with producer gas. Here the water and volatile hydrocarbons are eliminated, the product emerging as a comparatively light porous solid. It is then crushed, screened and elevated to storage bins, from which it may be fed by gravity to the retort charge containers. The screen undersize is fed back into the charge mixers.

No further description of the retort operation seems necessary, except to state that the carbon monoxide gas resulting from the reaction is mixed with an additional quantity of producer gas and then burned under the retorts to supply the necessary heat for the reaction. After cyanization, which requires about 13 hours, the charge containers are removed by an overhead traveling crane and cooled in cooling cans until the temperature has been reduced to about 100 deg. C. The material is then dumped on to a conveyor leading to the storage bins, the container is recharged and the operation repeated.

No detailed description of the leaching plant will be given. It is equipped with the requisite number of tanks, evaporators, crystallizers, centrifuges, presses, etc., all of this equipment being of standard make, easily obtainable.

In conclusion, I wish very briefly to mention one matter that will undoubtedly have a very important bearing on the success of this process. I refer to the use of the residual carbon in the leached furnace product as a decolorizing carbon and as a pigment. Realizing the strong probability that the "black liquor" carbon should represent an excellent raw material for the preparation of a decolorizing carbon and that its discolorizing qualities should be enhanced by its passage through the cyanizing reaction, a considerable amount of preliminary experimental work was undertaken to determine its value in this respect. Results thus far obtained indicate that a good decolorizing char can be prepared, and also that a carbon black may be obtained of a quality at least equal to that of a medium-grade black for pigment use. For this purpose about 1 lb. of carbon can be recovered for every 3 lb. of cyanide made. The influence which this phase of the subject has upon the cost of cyanide is, for obvious reasons, extremely important.

In closing, it should be stated that the development of this cyanide process is due to the ingenuity and efforts of a number of men among whom should be mentioned particularly Chas. B. Jacobs and Roger Williams.

Discussion

Mr. Moore: I would like to ask what effect sulphur would have in the black liquor.

Mr. Chickering: I don't really know; we haven't investigated what effect sulphur would have.

Mr. Moore: I mean in the form, not of sulphur, of course, but sulphates and in some cases possibly sulphides. I was thinking that in a sulphating process you would use the same as the sulphate process where you reduce some sulphate to sulphides, and the liquor is substantially the same.

SUPER SUBLIMED WHITE LEAD

By J. H. CALBECK

Read at the Pittsburgh Meeting, December 4, 1924

The manufacture of white lead is one of the oldest chemical industries, but not withstanding the long experience that engineers have had in the art, and the increasing production from year to year there have been few and relatively unimportant improvements made in the processes employed. The original basic carbonate white lead corroded by the old Dutch process still remains the leader from the standpoint of tonnage. Of course the patent files are full of improved processes for making white lead pigments, but the only ones to possess a commercial history of any consequence are the Carter, electrolytic and the sublimed white lead process. The two former produce a basic carbonate white lead of a chemical composition quite like the white lead corroded by the old Dutch process, while the latter produces a basic sulphate white lead. The sublimed white lead process was developed by E. O. Bartlett about 1876 at Joplin, Missouri, and consists briefly of producing a white fume by burning galena and other lead products with coke and flux in a very short stack furnace called a "slag eye" and cooling and collecting the white fume in bags. ("The Manufacture and Properties of Sublimed White Lead," John A. Schaeffer, *J. of Industrial and Engineering Chemistry*, Vol. 5, No. 2, February, 1913.)

There have been but minor improvements in this process, as in the case of any process that is continued over a long period of years, and although the engineering features of sublimed white lead have seen little change in thirty years, commercially the product has enjoyed a remarkable development. This development has come after years of observation and has shown basic sulphate white lead to be equal or superior to basic carbonate white lead for many purposes. Its principal use is in ready mixed paints, and the remarkable prosperity and growth of the paint industry all over the country has made an increasing demand upon the producers of basic sulphate white lead which was becoming difficult to meet.

New plants have been built from time to time. However, the question of meeting this increased demand by building additional sublimed white lead units as they had been for thirty years or of trying to develop an improved process for making sublimed white lead was settled by the following circumstances.

Although more than half the lead-bearing material used in the manufacture of sublimed white lead is galena, the additional lead by-products used are imperative to good production and good quality. There developed a critical shortage of these necessary by-products and it looked as if to increase production by the old process it would be necessary to use other lead by-products.

Since the war all pigment manufacturers have been improving the quality of their products greatly, and competition has improved the quality of all white pigments very noticeably in the past five years. Accordingly there grew up a demand for an extremely bright pigment and it seemed advisable to investigate the possibilities of improving the color of sublimed white lead. The problem then was simply to make an improved sublimed white lead by a process differing enough from the original one so that a different source of lead-bearing materials might be used.

It has long been known that lead fumes of almost any kind become sulphated to a basic sulphate of lead in the presence of sulphur dioxide gas. This principle has been used as a basis for a patent taken out by B. S. White of Joplin, Missouri, in 1916, whereby he proposed to manufacture basic sulphate white lead by converting litharge into a fume or vapor and mixing the fume with sulphur dioxide gas. So the problem before us seemed simple enough. All there was to do was to pass sulphur dioxide gas into litharge fumes or vapor and "presto" sublimed white lead would result. And theoretically this is all we have done. But the engineering problems encountered in bringing the process under absolute control in order to make the basic sulphate white lead of commercial quality, form the subject matter of this paper.

The preliminary work was done with a small experimental unit having a capacity of about fifty pounds per hour. Fig. 1 shows a diagram of the original installation. There are four important parts, the melting kettle, furnace, combustion chamber, sulphur burner and cooling and collecting systems. The heavy units were built on steel trucks to aid in moving about the laboratory. Since the principle of the process is the same in the small unit as in the large unit it will be discussed in connection with the small unit.

Refined corroders pig lead is melted in the kettle on the right and the molten lead is atomized by compressed air at forty pounds and projected into the furnace proper. Compressed natural gas at 15 lbs. per sq. inch is blown in with the compressed air and the air.

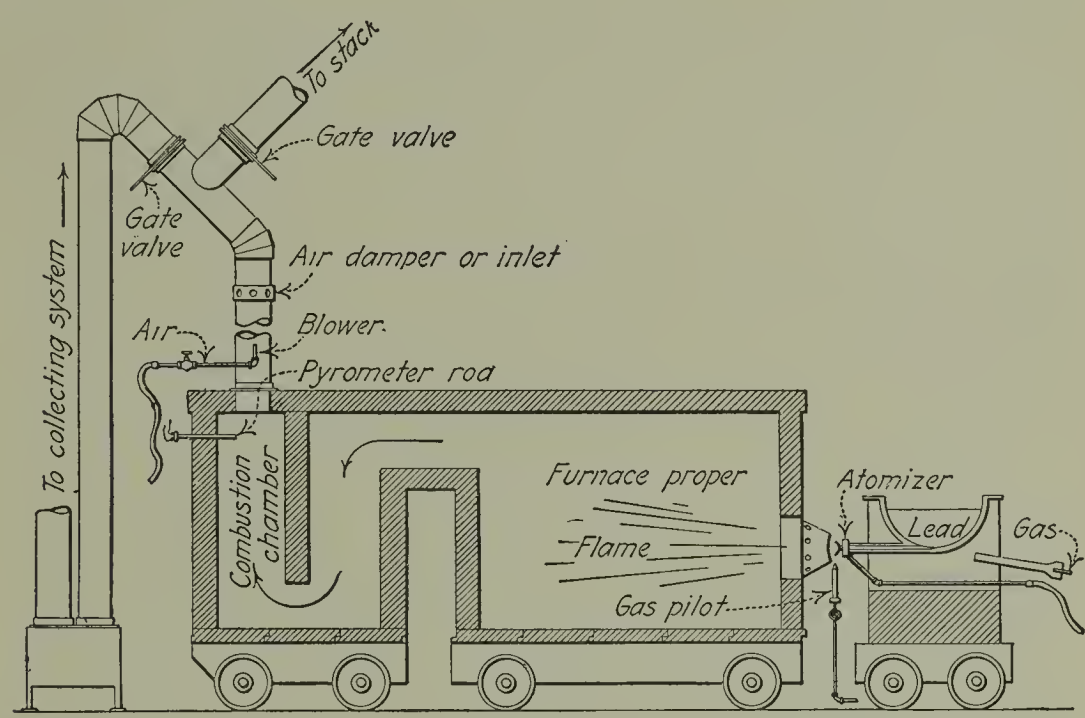


FIG. 1. Diagram of the Small-Scale Furnace for Lead Sublimation
An interesting feature in the construction of this experimental plant is the provision of steel trucks to aid in moving the heavy units about the laboratory.

The gas and finely divided lead burn in a long white hot torch-like flame. Now, sulphur dioxide gas is introduced at the point indicated as "gas pilot," the sulphur dioxide, natural gas, air and lead react to form the basic sulphate of lead. By changing the ratio of SO_2 to lead the chemical composition of the fume may be changed throughout wide limits. The fume as we prefer it consists of 25 per cent PbO and 75 per cent $PbSO_4$ in chemical combination having a formula of $PbO.2PbSO_4$.

Accurate control of the flame is necessary. If the flame is too rich in natural gas some carbon will be liberated and discolor the product. The combustion chamber gives the reaction time for completion and burns out the small amount of carbon that even a correct burner adjustment does not eliminate. The fume passes from the combustion chamber into a series of goose necks for cooling and is picked up by a fan and blown into the filter bags. The by pass stack is very essential as it may be opened quickly when the burner goes out of adjustment, thus preventing an off color product from going into the bags and spoiling what good material

may be there. The sulphur burner, not shown, was simply a steel cylinder with a blast fan at one end and an outlet pipe at the other. Molten sulphur was fed into the cylinder through a trap made of gas pipe. Our collecting system consisted of the goose necks shown in the picture, a fan, cyclone and small bag room. Fig. 2 is a photograph of the small experimental unit. The small experimental unit worked well from the start and we had little difficulty in making a pigment equal in appearance to our sublimed white lead.

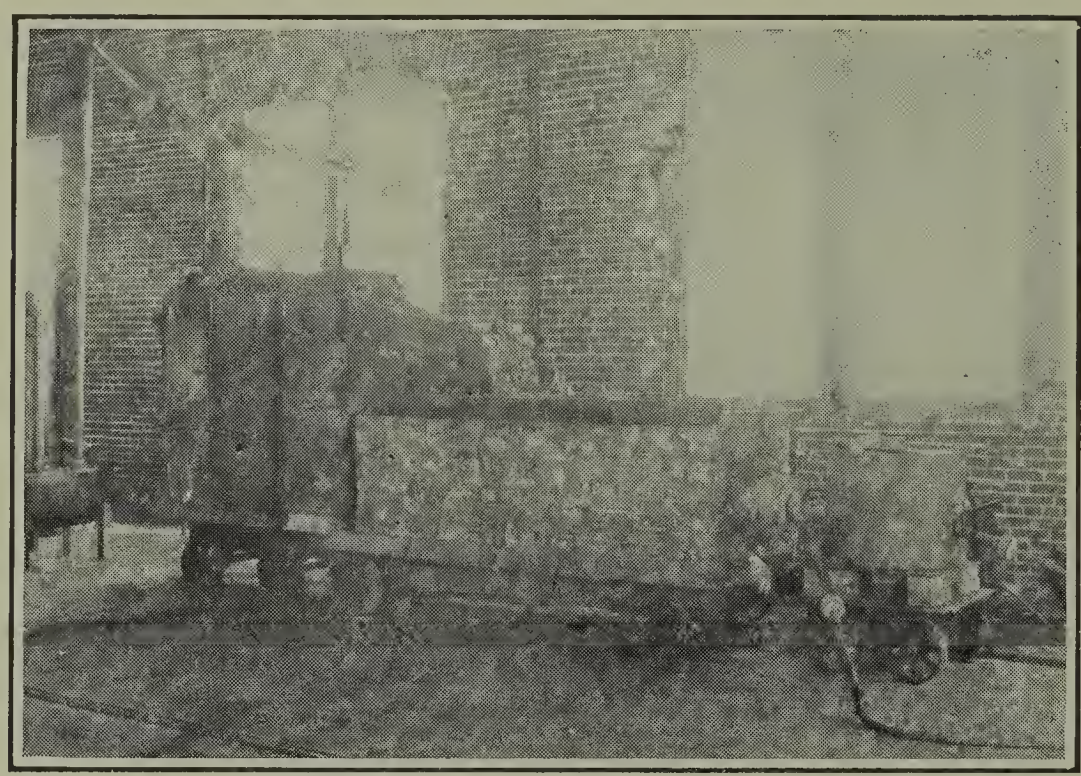


FIG. 2. The Experimental Furnace

Comparing this with the cross-section shown in Fig. 1 and the full-sized commercial unit in Fig. 8 shows how closely the original plan was followed in the final installation.

One day we opened the cyclone for a cleanout and imagine our surprise and delight when a veritable snow drift rolled out on the floor. Samples were taken to the laboratory and matched against our regular sublimed white lead and it was so much whiter as to make comparison ridiculous. Comparisons with French process zinc oxide and lithopone showed it superior to both in whiteness and brightness. The little plant was started up again and run until we had manufactured several hundred pounds of the new product, which we christened super sublimed white lead. This material was tested for color, covering power, fineness and opacity. Several hundred pounds were ground in oil and paints were made from it and tested, all with the result that we were instructed to proceed as rapidly as possible with a large commercial unit.

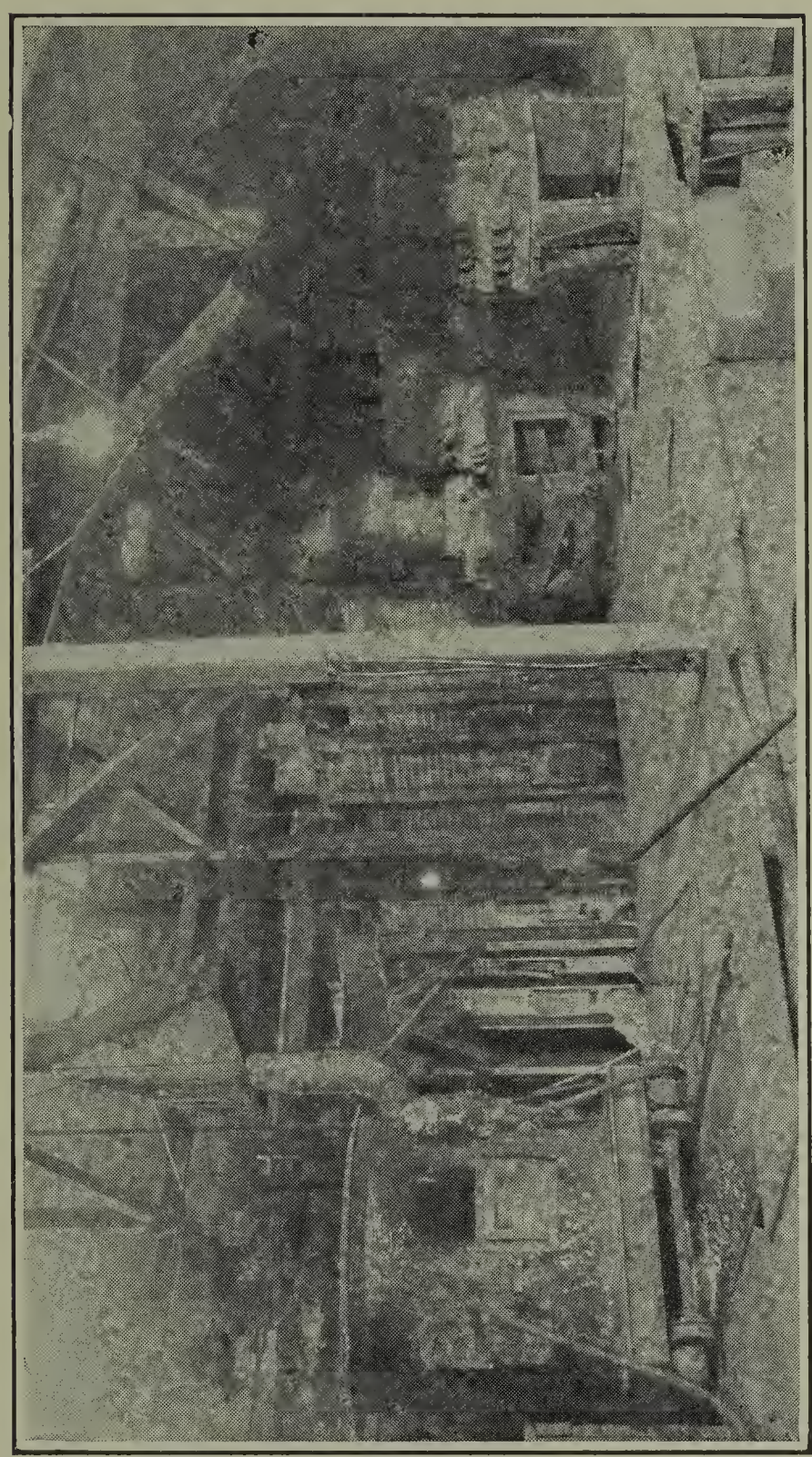


FIG. 3. One of the Melting Kettles in Position for Operation

The second of the three furnaces is to be seen at the right. These kettles are coal fired, since this fuel has been found preferable to natural gas for this particular operation. It will also be noted that the kettle is mounted on a truck, which permits its easy withdrawal for adjusting the burner or replacing parts.

The commercial unit which was installed consists of three large furnaces all connected to one long combustion chamber and has a capacity of 15 tons per day. Fig. 3 shows a photograph of the complete installation in operation.

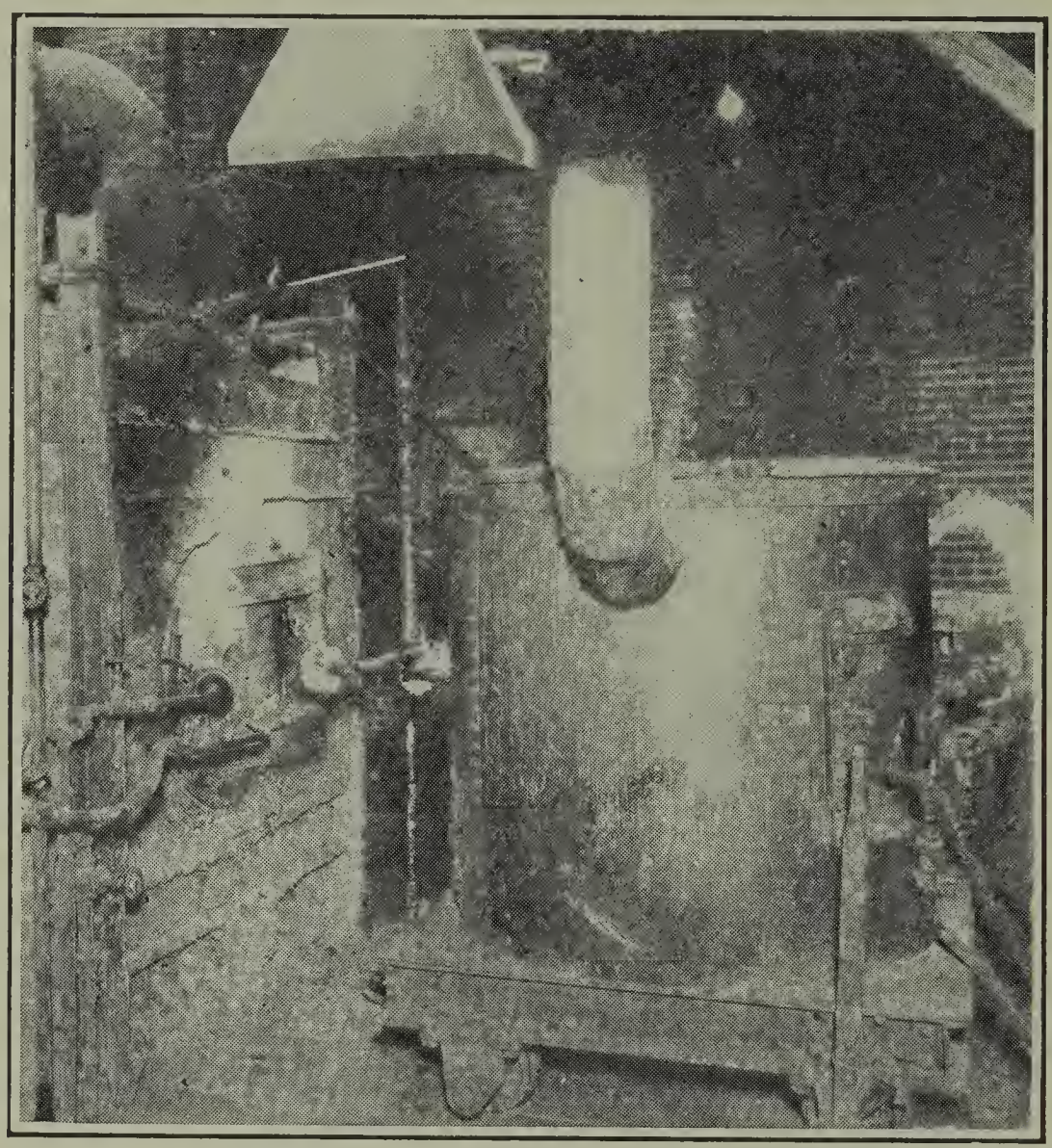


FIG. 4. Melting Kettle Withdrawn from the Furnace

The lead valve and the atomizer-burner may be seen bolted to the spout of the kettle. The sulphur fumes enter through the 8-in. cast-iron supply pipe directly above the furnace.

Fig. 4 shows the kettle withdrawn from its position directly in front of the furnace. The kettle is coal fired, for although we have an abundance of natural gas we find that a more uniform temperature may be maintained with coal than with gas, and correct temperatures are very essential for atomizing lead. The kettle which has a capacity of about three tons is mounted on a small truck which runs on a small track about 12 feet long directly in front of the furnace and in line with it. This arrangement is

essential in as much as the kettle and atomizer-burner must be withdrawn from their position in front of the furnace for adjusting or replacing atomizers, burners, etc. The kettle is easily moved forward and backward by the lever and ratchet attached to the rear axle. Bolted onto the spout of the kettle may be seen the lead

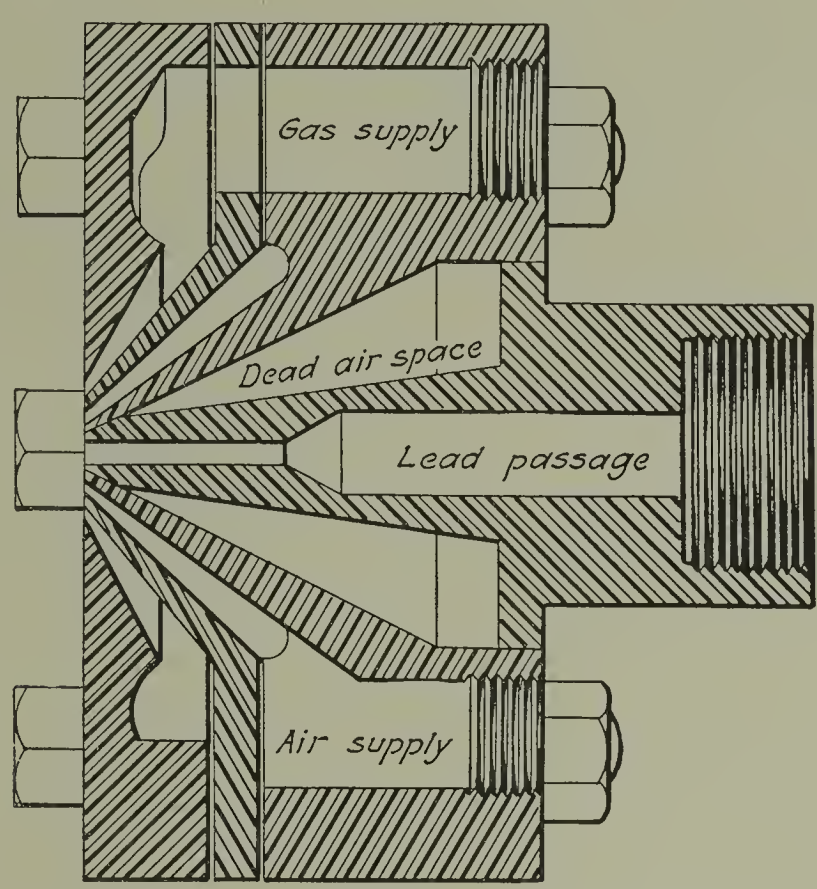


Fig. 5. A Cross Section of the Atomizer-Burner

The dead air space surrounding the lead passage proved to be the most effective means for preventing the freezing of the small stream of molten lead.

valve and the atomizer-burner. Fig. 5 gives a cross section of the atomizer-burner. The central member of the atomizer-burner is the lead nozzle. Surrounding it and separating it from the compressed air chamber is the dead air space. We were troubled for over a year by the atomizers freezing up. Although the atomizing air was preheated yet the expansion cooled the tip of the atomizer so rapidly as to freeze up the small stream of lead. After the development of the dead air space, the lead was insulated from the colder air and freezing up became very infrequent. The compressed air strikes the stream from all sides and reduces it to a fine spray which is easily volatilized and oxidized by the high temperature of the flame into which it is projected. Outside of the air supply and concentric to it is the gas supply. In the early stage of this process we attempted to use gas at low pressure but the flame

was blown so far back into the furnace as to be very inefficient. Forcing the gas into the air stream at 15 pounds pressure gives a better mixture with the result that the flame burns back within a few inches of the tip of the atomizer.

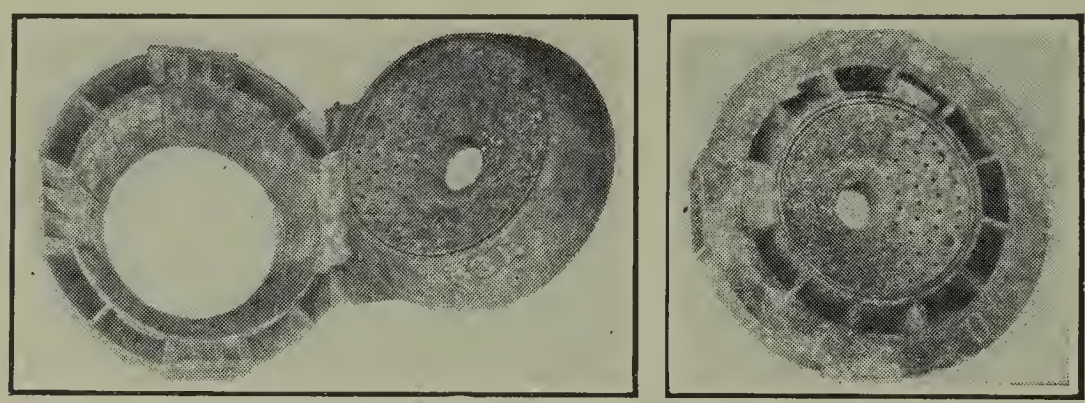


Fig. 6. Two Views of the Pilot Burner of the Sublimation Furnace

At left the burner is open for cleaning, at right is its appearance if viewed from inside of the furnace. The atomizer burner fills the large center opening, the gas flames issue from the small openings, four of the rectangular openings in the periphery are for air and eight are for sulphur dioxide.

Returning to Fig. 4 a large casting may be seen set in the brick work of the front of the furnace directly in front of the atomizer. This casting is the pilot burner and sulphur dioxide port. The sulphur dioxide gas is delivered to this casting by means of the 8 inch cast iron supply pipe. The simple gate valve for control of the sulphur dioxide supply may be seen to the left of the elbow. Fig. 6 shows the pilot burner swung open for cleaning and also shows how it appears if viewed from the inside of the furnace. The atomizer-burner just fills the large hole in the center. Gas flames issue from all the small holes in the central number. All but four of the large rectangular openings in the outside member admit air. These four which are opposite the projections in the casting admit the sulphur dioxide gas.

The furnace and combustion chamber are brought up to the proper temperature by this pilot burner, the gas from the furnaces passing out through a by-pass stack similar to the one on the small unit. (See Fig. 1.)

Pig lead having been melted and brought to the proper temperature in the kettle the lead is turned on by the lead valve and its flow properly adjusted before the air is turned on. The lead runs out in a small stream about one eighth inch in diameter and is allowed to fall on the floor until the proper adjustments have been

made. Now the kettle is wheeled forward by means of the lever and ratchet. The atomizer-burner passes through the hole in the center of the pilot burner. This brings the kettle to the position

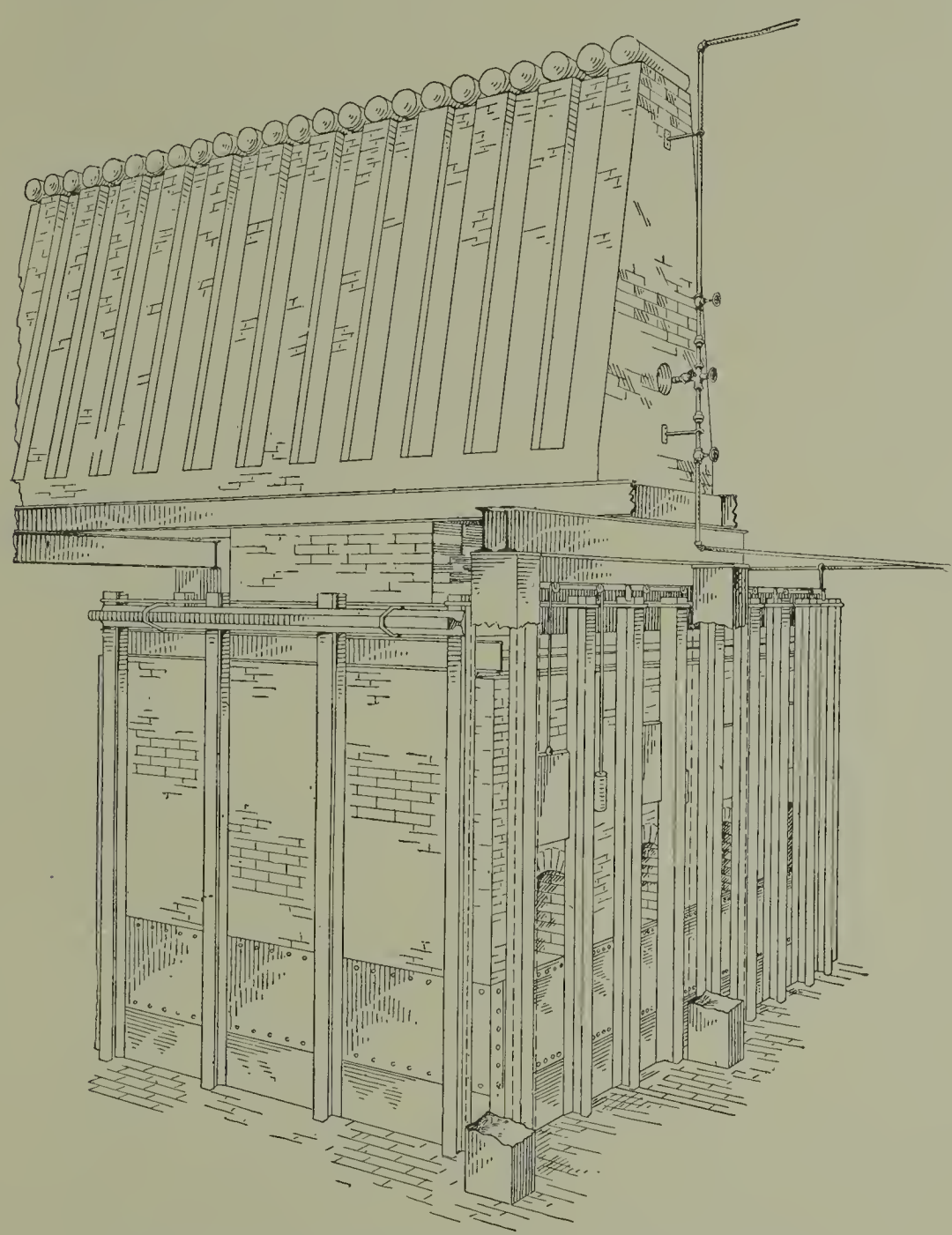


FIG. 7. Sketch Showing Furnace Construction

The four clean-out doors on the side of the furnace proper are clearly seen in this drawing. So, too, is the large outlet at the top that opens into the combustion chamber overhead.

shown in Fig. 8. The air and gas are turned into the atomizer-burner and formation of supersublimed white lead is instantaneous. The operator or "front man" adjusts the gas in both the pilot burner and atomizer-burner, and the air in the atomizer-burner until the flame produced is of the proper color and length. One

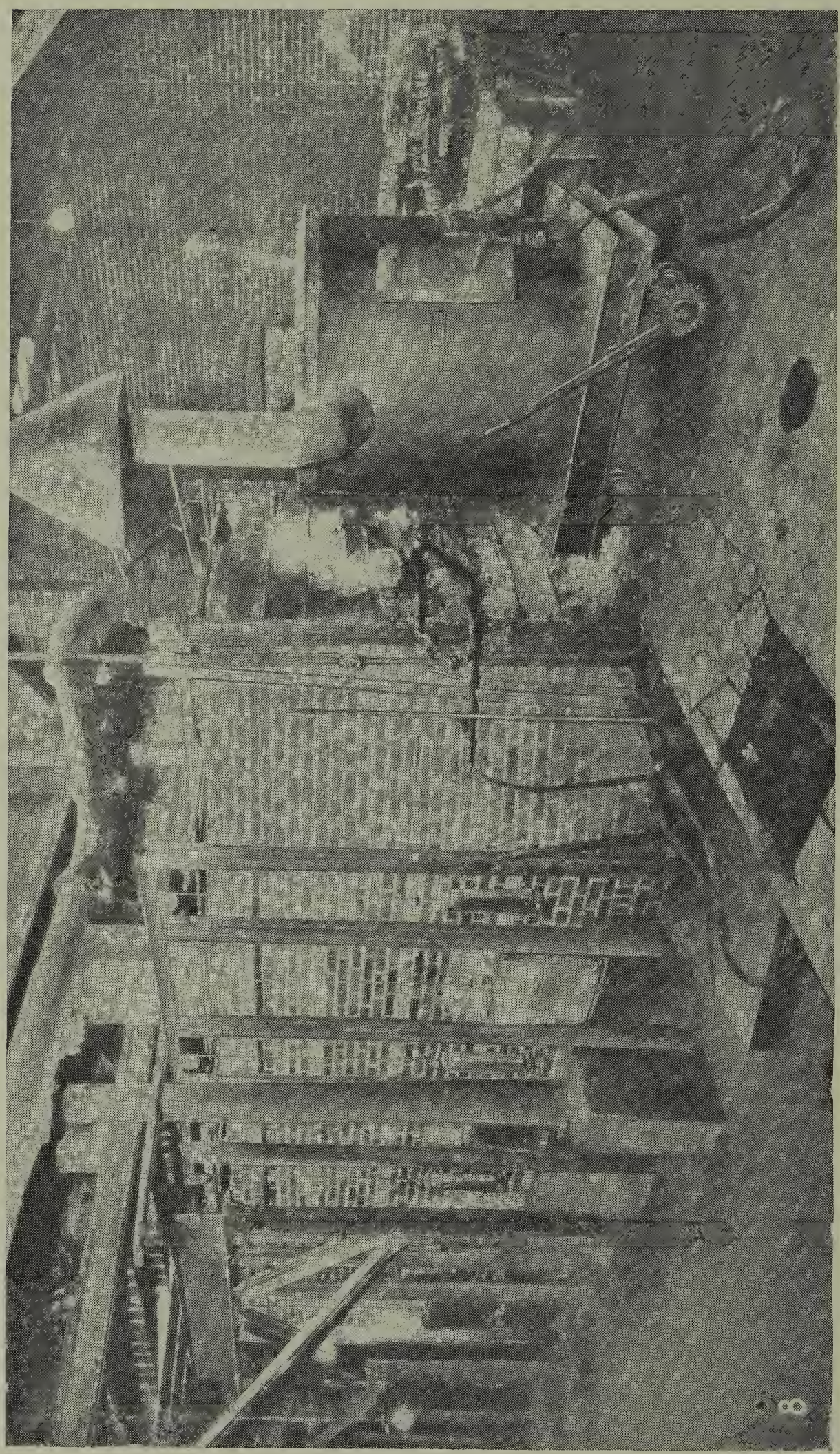


Fig. 8. The First Commercial Unit for Super Sublimed White Lead
The melting kettle, holding 3 tons of molten lead, is mounted on a truck in order that it may be easily withdrawn for adjustment.

front man watches the three furnaces. He has two helpers to keep the kettles supplied with lead and properly fired. Occasionally a burner goes out of adjustment and the kettle is wheeled back and the atomizer-burner trimmed and re-adjusted. The atomizer-burners have to be removed once or twice a day and thoroughly cleaned and reassembled. Both the gas and the air are pre-heated before passing into the atomizer-burner. Coils of pipe are set in the walls of the fire boxes under the kettles and used as pre-heaters. The two lengths of hose leading into the back of the kettle (Fig. 8) supply the air and gas to the pre-heater coils.

The furnace proper has a large rectangular basin 22 ft. x 8 ft. and is 8 ft. high. There are four cleanout doors on each side and an outlet hole in the arch at the back which opens into the combustion chamber overhead. The important feature of the furnace is the lead basin which forms the floor of the furnace. This basin is of boiler plate lined with brick and contains a bath of lead about 10 inches deep. The heat of the furnace keeps the bath molten and the oversize uncombined material from the atomizer falls and floats on the surface of the molten bath and is easily raked off through the cleanout doors once a day. The amount of this cleanout depends upon the care and skill with which the atomizer-burner is adjusted. In a year's time we have developed some very expert "front men," who manage to keep this cleanout down to a reasonable figure, although for a long time the amount of this cleanout was one of our chief difficulties.

From the furnace proper the fume passes into the long brick trail overhead which acts as a combustion chamber. Pyrometer control is maintained on each furnace and upon the fume as it leaves the combustion chamber. The draft in the furnace which is provided by the suction fan that carries away the fume must be carefully adjusted and recording draft guages are used in this control. The fume from the combustion trail passes directly into a large cyclone. The cyclone separates out a small amount of heavy material such as scale from the sides of the combustion chamber and furnace and any uncombined lead that may carry over during periods of bad adjustment. From the cyclone the fume passes through the cooling goose necks, into the fan and then into the bag room. Fig. 9 shows the cooling system or goose necks. Fig. 10 shows the filter bags and Fig. 11 shows the hoppers under the bags into which the finished product falls.

The sulphur burner is an extremely simple affair and no doubt would seem crude to one experienced in burning brimstone for acid manufacture, but it fits our need exactly. It consists of a rectangular furnace 16 x 4 x 4 feet built underground and covered with earth. The sulphur is fed through a deep kettle which is mounted in the arch of the furnace. A hole in the bottom of the kettle and a

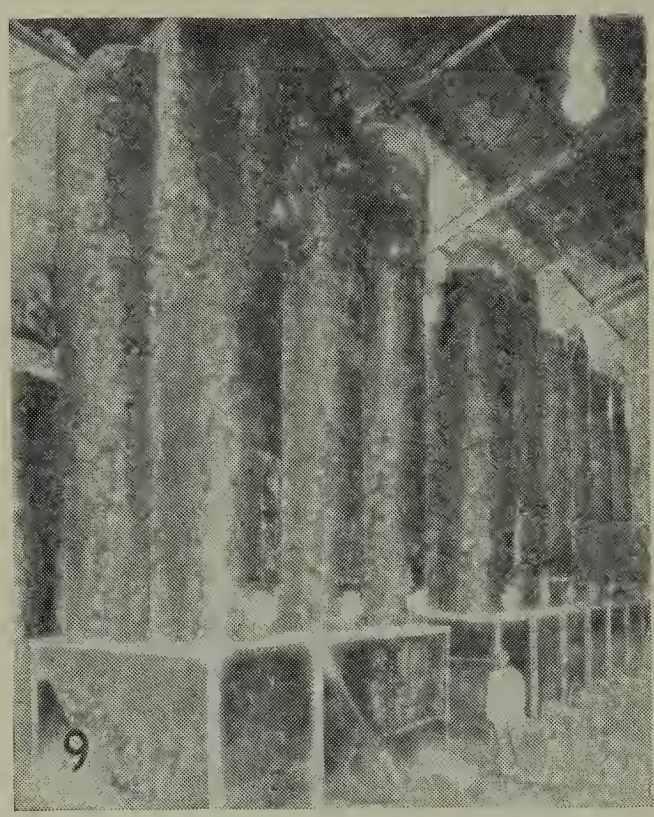


Fig. 9. The "Gooseneck" Cooling System for Sublimed Lead Pigment

From the cyclone separator that removes heavy scale and other impurities, the lead fumes pass through these coolers to the fans and bag filters.

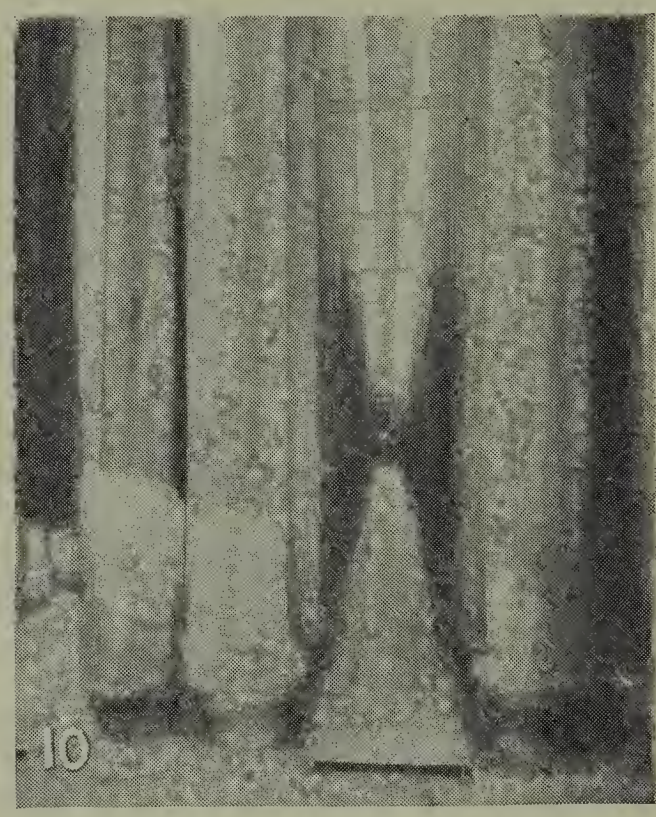


Fig. 10. An Aisle Through the Filter Bags in the Bag Room

The sublimed pigment is here sepa-separated from the lead fume.

conical cast iron plug constitute the valve. The heat from the furnace keeps the sulphur in the kettle molten and by adjusting the plug in the hole by means of a lever on top of the kettle a uniform supply of sulphur is afforded. Air is supplied from a blast fan into one end of the furnace. The sulphur fume passes out the other end through a water jacketed section of cast iron pipe. Only sufficient air is admitted to keep the sulphur fume in the vapor phase. Complete oxidation of the sulphur is not desirable because it seems that the more sulphur vapor we can feed to the burner without it condensing and running down into the burners the better results are obtained. The sulphur fume is conducted to the three

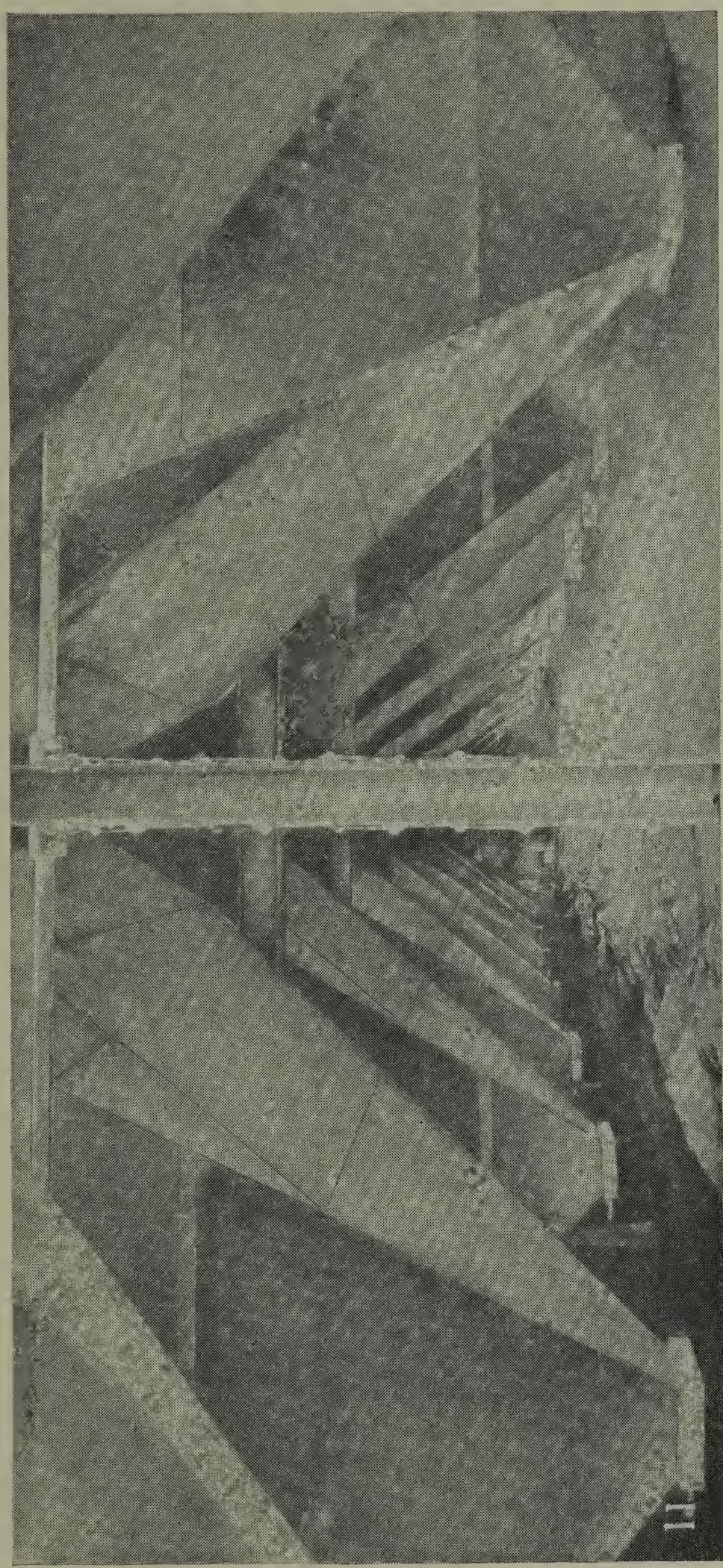


FIG. 11. Hoppers Beneath the Filter Bags

It is here the finished product, "super sublimed white lead," is finally removed from the manufacturing process.

furnaces by the long cast iron supply pipe seen above the furnaces. (See Fig. 3.)

This then describes the construction of the unit and some details of the process for making super sublimed white lead. As suggested earlier, the striking thing about this new pigment is its appearance.

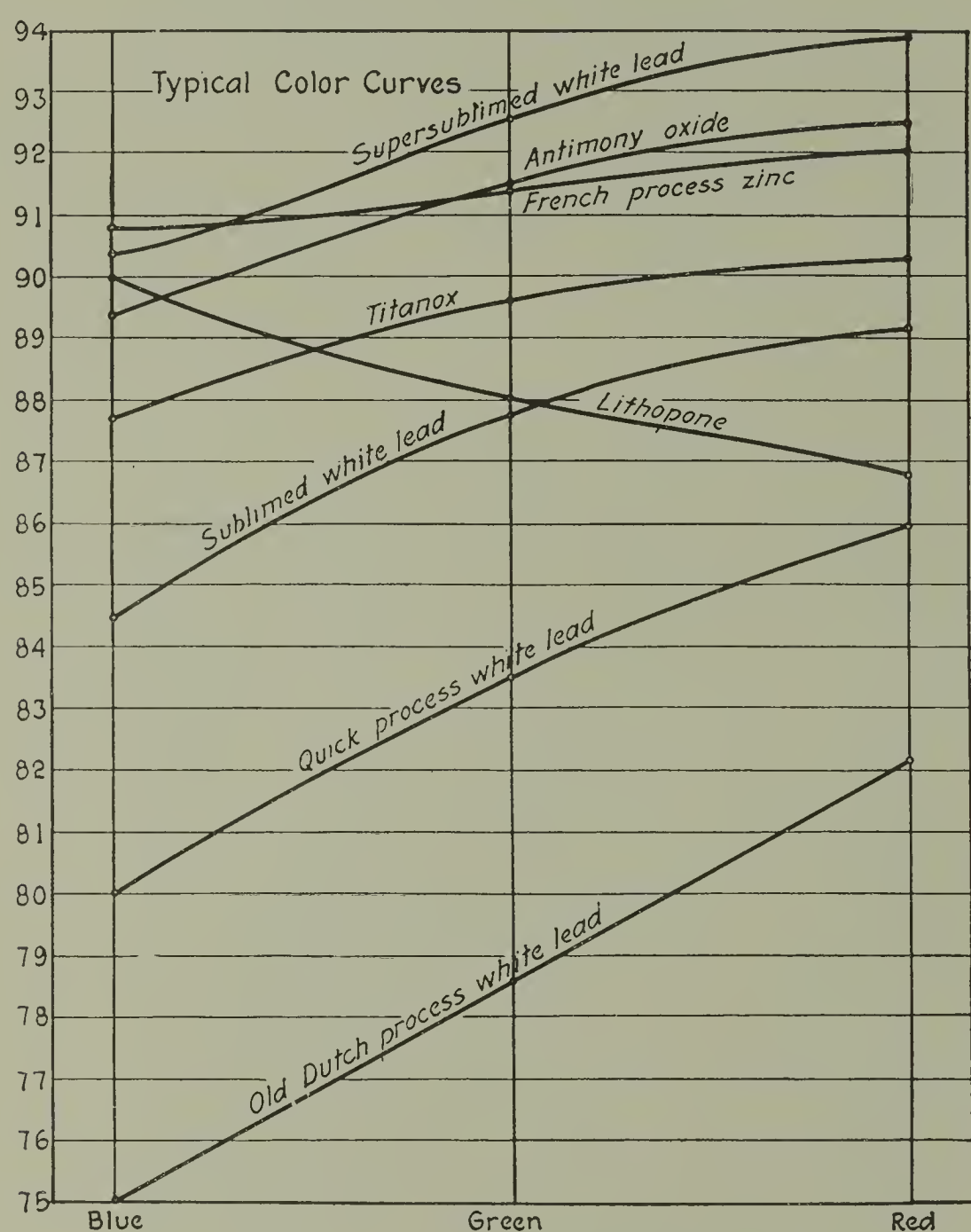


FIG. 12. The Brightness and Whiteness of the New Pigment Compared with the Other Typical Products

Fig. 12 shows a comparison chart on some typical white pigments. The lines indicate both the brightness and whiteness of the pigments. The more horizontal the line the whiter the pigment, and the higher on the chart the brighter the pigment. At the top is to be found super sublimed white lead, then close to it, its only rival French process zinc oxide. Then follow the other commercial white

pigments in the order of their brightness and whiteness. Fig. 13 shows a micrograph of the pigment magnified 2,000 diameters. It has a particle size of about .7 microns. Its behavior in oil and covering power are equal or superior to any other lead pigment and its durability promises to equal the other white leads in as much as the product is so similar to sublimed white lead which has stood the test of time.

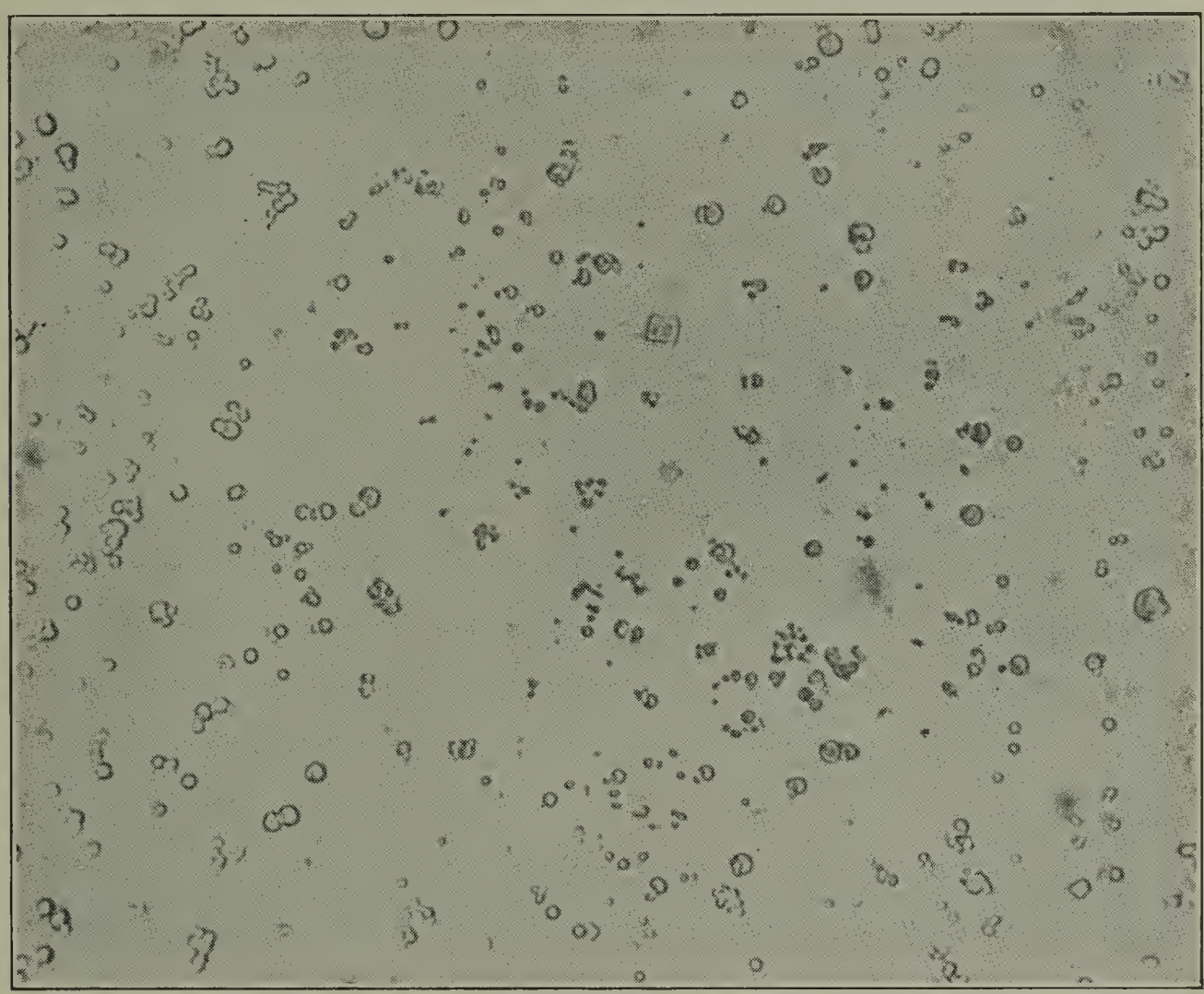


FIG. 13. Photomicrograph of Super Sublimed White Lead

The first experimental work on this pigment was begun two years ago in October and the large unit began operation a year ago in October, and now the plant has been in successful operation for over a year with less than 60 days shut down for repairs or awaiting orders for the product. The design and construction of operation of this process has been done by Dr. J. A. Schaeffer, Mr. B. S. White and myself, all of The Eagle-Picher Lead Co., and we are well pleased with the results of our efforts on super sublimed white lead.

ELECTROLYTIC CALCIUM ARSENATE

By STEWART J. LLOYD, and A. M. KENNEDY

Read before Providence meeting, June 25, 1925

Arsenic appears in insecticides in two forms, as trivalent arsenic in the arsenites and as pentavalent arsenic in the arsenates. Generally speaking, the arsenites are cheaper and more toxic than the corresponding arsenates and would be widely used were it not that they are much more dangerous and are destructive to foliage. As the raw material from which practically all arsenic compounds are made is common, white arsenic (As_2O_3), some means of oxidizing this to the pentoxide (As_2O_5) form must be adopted if the arsenates are to be made.

Until quite recently only one method of effecting this oxidation was practiced, the nitric acid process, in which the white arsenic is heated with strong nitric acid. As the nitric acid is reduced in this operation to oxides of nitrogen and since the cost of oxidation would be prohibitive if these oxides were lost, a regenerative tower system is invariably provided to reconvert these nitrous fumes to nitric acid. This is an item of considerable magnitude in plant cost. Moreover, to withstand the action of hot nitric acid and its fumes, earthenware, duriron or aluminum containers and conduits must be provided which are costly and on which repairs and depreciation form a considerable item in plant operation. On account of the presence of nitrous fumes, working conditions, in some instances at least, are far from pleasant.

The oxidation by chlorine of white arsenic suspended in water has been proposed, and has been tried in Italy and in at least one plant in this country with results which are not known to the writers.

During the early part of 1923, when there was expected throughout the South a large shortage of calcium arsenate, the Alabama Power Company, operating in the heart of the cotton belt and dependent for its prosperity on the prosperity of the cotton farmer, adopted the suggestion of one of its engineers that a study be made to determine whether an electrolytic process could be devised for the oxidation of white arsenic which would lower the cost of pro-

duction of calcium arsenate, provide a local and convenient source of supply of this material for the cotton farmers and secure an additional power consumer for the Company.

The preliminary experimental work was carried on, first at the plant of the Federal Phosphorus Company at Anniston, Ala., where it was found that white arsenic could be oxidized electrolytically with very simple laboratory apparatus and later at the University of Alabama where it was shown that the electrical or current efficiency of this oxidation was high. The General Electric Company, having heard of the work, offered the facilities of its Research Laboratory at Schenectady where it was shown that the process could readily be reduced to a commercial state since, except for the electrolytic cells, stock chemical apparatus could be employed throughout and further that these cells presented no great difficulty in design and should therefore be constructed readily and cheaply.

Although all the cost of the research work was born by the Alabama Power Company, all of the patent [1] rights were disclaimed by it and were left entirely to the inventors.

Outline of the Process

White arsenic is dissolved in caustic soda in the proportion of 198 : 250 parts to form a basic, sodium arsenite solution. When this is electrolyzed between iron electrodes, hydrogen and a small amount of metallic arsenic (about 1 per cent of the As_2O_3 used) are produced at the cathode, only a very small amount of oxygen being evolved at the anode, the remainder serving to convert the sodium arsenite to arsenate.

When the oxidation is completed, the solution is filtered to separate the metallic arsenic and the filtrate added to a suspension of calcium hydroxide. The sludge is filtered and the precipitate of calcium arsenate, washed and dried. The filtrate of caustic soda, after being concentrated, may be used to dissolve fresh arsenic. The raw materials are therefore white arsenic, hydrated lime and sufficient caustic soda to replace the inevitable losses of the operating cycle.

It has been shown that the use of purified, white arsenic (99 per cent As_2O_3) which is required with the nitric acid process, is not necessary with this process, but that the unpurified, first roast, precipitate or gray arsenic (90–95 per cent As_2O_3) may be used,

[1] Patent No. 1,517,516 of Dec. 2, 1924.

thus saving the cost and losses in re-roasting the arsenic to purify it.

The sequence of changes may be represented by the following equations;

1. $As_2O_3 + 6NaOH \rightarrow 2NaAsO_2 + 4NaOH + H_2O$

2. $2NaAsO_2 + 4NaOH + (\text{current}) \rightarrow 2Na_3AsO_4 + 2H_2$

3. $2Na_3AsO_4 + 4Ca(OH)_2 \rightarrow (CaO)_4As_2O_5 + 6NaOH + H_2O.$

It will be noticed that the proportion of lime to sodium arsenate used does not produce the tri-calcium arsenate known to the chemist. The extra molecule of lime is used to produce a commercial article in which the water solubility of the As_2O_5 is sufficiently low to avoid any danger of "burning" or injuring the foliage of the cotton plant.

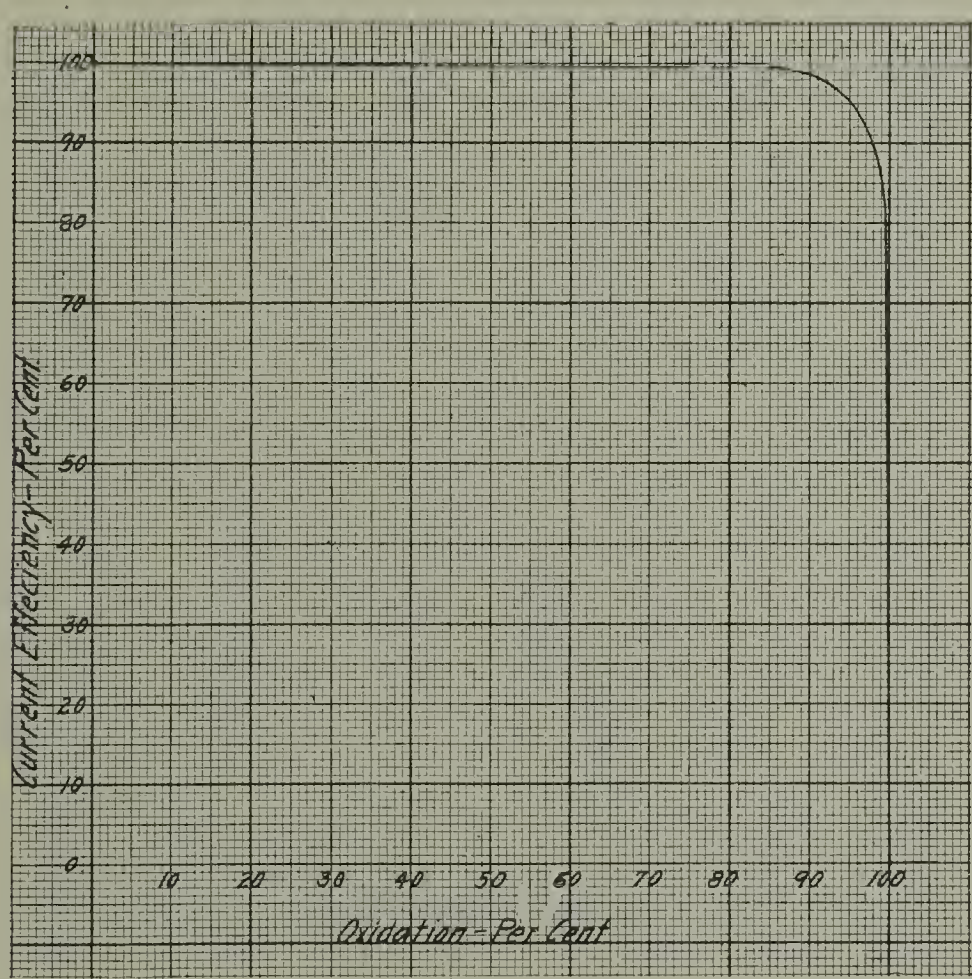


FIG. 1

Figure 1 shows a current efficiency—oxidation curve obtained at the General Electric Company's Research Laboratory. It will be observed that for the first 85 per cent of the oxidation, the current efficiency is practically 100 per cent while over the whole range of oxidation, this efficiency is about 85 per cent.

For the benefit of those who have to provide laboratory exercises for students, it may be worth noting that the writer has found this electrolytic oxidation of sodium arsenite very satisfactory.

Plant Operation

During January, 1924, the Gulf States Chemical and Refining Company of Birmingham, Ala., was reorganized to operate this process commercially. When, on February 1, work was actually begun, it was questioned whether a plant could be erected, equipped and started in operation in time to produce calcium arsenate in time to use for the 1924 cotton crop.

To assist in this work, the Alabama Power Company offered the free use of one of its reserve steam plants at Montgomery, Alabama, together with any useful equipment in the shape of boilers, motor-generators, switchboards, etc., which it contained and to remove from the plant all equipment that was useless for calcium arsenate production. Two 150-horse-power boilers and four motor-generator sets with a combined capacity of 1,000 kilowatts, which had been used for street car service, together with their switchboard equipment, were retained. The use of these motor-generators, producing direct current at 600 volts, necessarily influenced the design of the electrolytic cells.

This plant is of brick, about 120 x 180 ft., divided by fireproof walls into three parts which were originally, from west to east, a boiler room, an engine room and a switchboard room.

The original boiler room, having trackage, was equipped for raw material storage, for the mixing of solutions and the precipitation of calcium arsenate. The old engine room containing the motor-generators, was equipped with electrolytic cells, storage tanks, filter presses, dryer and pulverizer. The original switchboard room could not be cleared out in time for 1924 production but will be used for finished material packing and storage. A transformer shed on the east side of the plant, to which trackage can be readily obtained, will be converted into a shipping platform with a capacity for loading two to three cars at a time.

Figure 2 is a flow sheet showing the course of material through the plant and figure 3 shows the arrangement of the chemical apparatus.

In plant operation, a 10 per cent solution of caustic soda is made up in a 6,000-gallon horizontal tank (No. 1) fitted with a

vertical sump pump. As it is necessary to make up a large amount of solution only when starting the plant in operation, it has been found convenient to make up the small amount needed to replenish the daily loss due to leakage by placing the solid caustic in a large

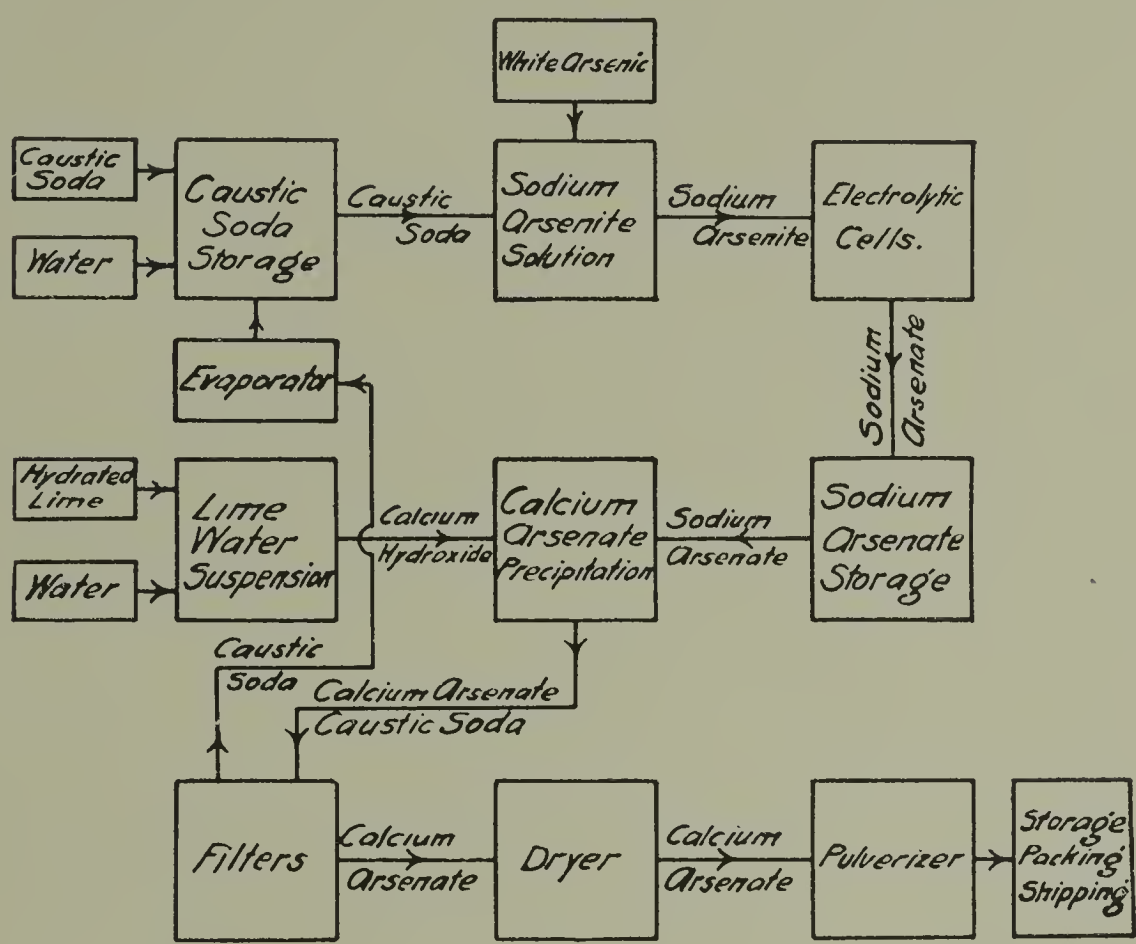


Fig. 2

pan discharging into the rear of the horizontal tank and circulating the contents of this tank over the caustic by means of the sump pump until solution is complete. By this means, a uniform mixture is provided and the stratification of layers of solution having different densities is avoided.

In making the mixture of sodium arsenite in tank 5, precautions were necessary to prevent the danger of poisoning the operatives with arsenic dust. This tank is closed on top by the charging platform, and to carry off any dust which may occur, is connected with the boiler stack which, in this plant, is unusually large. To prevent dust, the arsenic is removed from the keg as a liquid by providing in the platform floor a grating in the center of which is a nozzle connected to the caustic soda sump pump of tank No. 1. In handling the white arsenic, the friction bung in the head of the keg is removed, the keg inverted over the grating and caustic soda

pumped through the nozzle until the keg is emptied and cleaned. When a sufficient amount of arsenic to make up a batch has been added to the tank in this manner any additional caustic soda solution required to give 1 part of As_2O_3 to 1.25 parts of NaOH is run directly into the tank. The agitator is then started and kept running to insure thorough mixing.

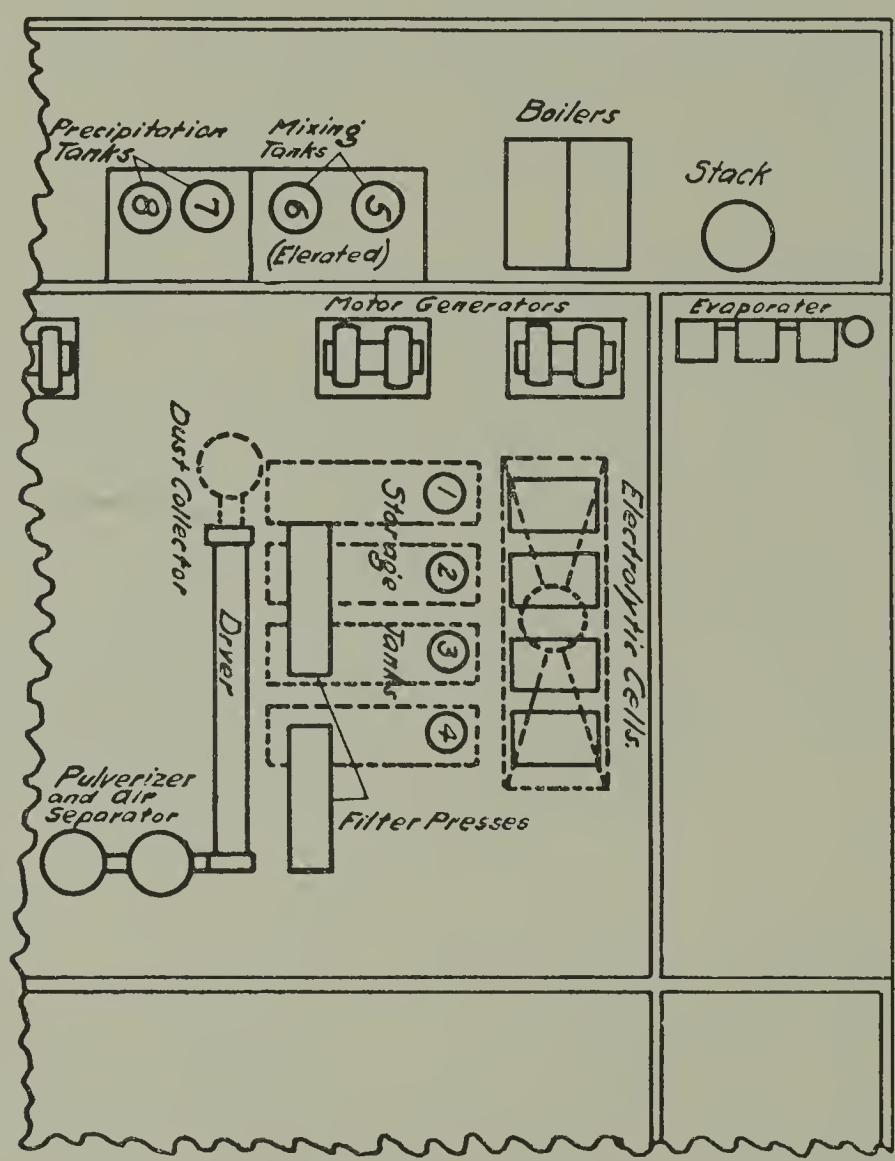


Fig. 3

From the mixing tank, the sodium arsenite solution is conveyed to the electrolytic cells by gravity.

It had been determined from laboratory work, that 30 amperes per sq. ft. of single electrode surface could be used with sheet iron electrodes through a solution of sodium arsenite without over heating and that to produce this current density required about three volts per cell and that the plates could be used as bi-polar electrodes.

As the motor-generator sets acquired from the Alabama Power

Company produced direct current at 600 volts, it was necessary to design the cells so that 200 plates could be used in series.

The final cells consist of boxes or vats 8 ft. 6 in. long, 5 ft. wide and 4 ft. deep, made of Alabama marble, 4 in. thick and slotted on 1 in. centers to receive 101, $\frac{1}{16}$ in. iron plates each having 7 $1\frac{1}{2}$ in. holes through one of the short ends and assembled so that these holes were consecutively on opposite sides. This marble was selected by plant Superintendent W. F. Nagel after a series of tests to determine a material which would withstand the action of hot, caustic soda solution and at the same time retain its insulating quality.

The sodium arsenite solution is admitted at each end of the cell and is returned from the center. This return is piped to a 6,000-gallon tank (No. 2) and when the mixing tank (No. 5) had been emptied, is kept circulating through the cells and tank No. 2 by means of the sump pump until oxidation is 99 per cent complete as shown by analysis. When this is accomplished, the finished sodium arsenate solution is transferred to storage tank No. 3.

Care is taken not to empty the cells completely, as it has been found that, while the admixture of arsenate solution with the arsenite lowers the current efficiency of oxidation slightly, it reduces the reduction of metallic arsenic on the cathodes very materially.

A suspension of 20 per cent hydrated lime in water is made in mixing tank No. 6 which is provided with an agitator and with live steam for heating. A known weight of lime in this suspension is allowed to flow by gravity into tank No. 7 or No. 8 and an amount of sodium arsenate solution added from tank No. 3 so that the weight of CaO will practically equal that of the As_2O_5 to produce a final product which will contain about 42 per cent total As_2O_5. These tanks are provided with agitators which are kept in motion as long as there is any mixture in the tank.

Care has to be used in making this mixture. With hot solutions, the precipitate of calcium arsenate is coarse and will not bulk high enough to meet the specifications of the U. S. Department of Agriculture—80 to 100 cu in. per pound. If the mixture is too cold, the reaction is so slow that production is diminished and the other operations delayed.

When, by analysis, the reaction is shown to have been practically completed, the sludge is pumped through a 36 x 36 in. 35 plate Sperry Filter Press, equipped for thorough washing. Two of these are provided.

The filtrate of dilute caustic soda solution is drawn off into storage tank No. 4. It has been found that the excess of calcium hydroxide contained in commercial calcium arsenate is not soluble in caustic soda solution even when very dilute but is of course slightly soluble in water to which it gives the familiar "milk of lime" appearance. When the filter press is filled the sludge pump is stopped and water forced through the cake to remove the caustic soda. As long as this wash water runs clear it is conveyed to the dilute caustic soda tank No. 4; as soon as it becomes milky it is conducted to the sewer and the wash continued for about five minutes to insure the complete removal of caustic soda.

The filter cake is conveyed to a 5 x 35 ft. Louisville Rotary Steam Dryer. Some difficulty was experienced here in calcium arsenate building up on the heating coils and in dust loss from the stack. These difficulties were overcome by Mr. Nagel, the first by suspending a loose chain in the center of the dryer which by continually falling freed the steam pipes of accumulation and the second by a washer for the stack gases.

The calcium arsenate usually leaves the dryer as a fine powder but to insure a product which will bulk between 80 and 100 cu. in. per pound a bucket conveyor is arranged to deliver the dryer discharge to a Raymond Pulverizer and Air Separator the fan speed of which is adjusted so that the product discharged will come within the above specification. A small amount of lighter product is carried over and discharged in the stocking collector.

The dilute caustic soda solution is pumped to a Swenson Triple Stage Evaporator where it is converted by steam from the pumps into a 10 per cent solution and pumped to the caustic soda storage tank No. 1. The loss of caustic soda from leakage and washing amounts to about 5 per cent of the amount used per cycle of 24 hours.

When operating at full capacity of 10 tons of calcium arsenate per day, about 60,000 cu. ft. of hydrogen are produced. To prevent danger from the explosion of this, the electrolytic cells are provided with a sheet iron hood and 24 in. vertical stack which thoroughly ventilates the cells and the area around them.

Chemical Control

The specifications of the U. S. Department of Agriculture provide that commercial calcium arsenate must contain at least

40 per cent total As_2O_5 of which less than .7 of 1 per cent shall be water soluble and that the product, when measured after having had a current of air passed through it, shall bulk between 80 and 100 cubic inches per pound.

In addition to the analysis of raw materials and finished product, a thorough chemical control is maintained throughout the process to insure a product which will fulfill the above specifications and when reasonable care is taken in the control of the dilution and temperature of the precipitation tanks, no great difficulty has been experienced in this.

One observed quality of calcium arsenate produced by the electrolytic process as compared with that of the nitric acid process may be worthy of mention. This material is usually dusted on the cotton plants at night so that the heavy dew which usually occurs in the South will seal the dust to the plants. When applied at this time, no difference can be noted between the sticking quality of nitric acid or electrolytic calcium arsenate. When applied during the heat of the day when there is no dew on the plants however, a great difference has been noted between the sticking qualities of the two products. Agitation of the plant or a few hours of wind will usually remove practically all of the nitric acid product applied at this time while the electrolytic product has been found to adhere very much better. In one specific instance, during a dry weather spell of August 1924, adjacent rows of cotton were dusted with the two products about noon. On the next day the nitric acid product had apparently disappeared, while sixteen days later, leaves were collected from the row dusted with electrolytic calcium arsenate which still retained a noticeable quantity of the product.

Other Arsenates

Since the novelty in this process consists in the method employed to convert arsenic trioxide to arsenic pentoxide, it would be expected that other arsenates as well as that of calcium might be manufactured also. Up to the present only calcium arsenate has been made commercially, but small scale production of lead arsenate encountered no serious difficulty. A crystallizer has recently been added to the equipment, so that sodium arsenate may be obtained likewise.

SYNTHETIC GYPSUM—ITS RECOVERY AND USE

By ROBERT S. EDWARDS

Read and Discussed at the Providence Meeting, June 26, 1925

Plaster of Paris is produced on an extensive scale in the United States by the partial dehydration, under suitable conditions, of the natural mineral gypsum, which is a hydrated calcium sulphate having the formula $CaSO_4 2H_2O$.

In addition to the natural occurrence of the hydrous calcium sulphate as the mineral gypsum, it appears as a by-product in certain chemical operations which can be generally characterized as reactions between calcium salts and sulphuric acid. More specifically the sources from which synthetic gypsum is produced fall under two heads.

a. The actual treatment of calcium bearing minerals or salts with sulphuric acid for the purpose of producing other acids, such as phosphoric acid, which is manufactured by treating rock or bone phosphate of lime with sulphuric acid and acetic acid from the treatment of acetate of lime with sulphuric acid.

b. The precipitate formed as the result of neutralizing solutions containing free sulphuric acid with some form of a lime salt, usually the pulverized carbonate of lime.

In both of these reactions the residual product is a precipitated hydrous or semi-hydrous calcium sulphate.

Thus, as briefly stated, synthetic gypsum is being produced each year in the United States at a rate that exceeds 400,000 tons and this considerable yearly tonnage seems destined to show a steady increase as time goes on. When we consider that for every ton of synthetic gypsum produced as waste a definite power and labor expenditure becomes necessary to remove such waste to the dump, the problems involved in converting it to a marketable product are worthy of careful consideration.

Of the total amount of synthetic gypsum produced yearly in the United States, approximately 85 per cent is obtained by the treatment of either rock or bone phosphate of lime with sulphuric

acid in the production of some form of phosphoric acid or its several salts.

In the specific case of phosphoric acid manufacture the precipitated gypsum accumulated thereby approximates the same tonnage as the crude rock or bone phosphate of lime so treated; the waste gypsum being conveyed to the dump either by belt conveyor, or pumped in slurry form through wood stave pipe.

Problems Involved in the Conversion Process

The process for treating this waste synthetic gypsum and converting it into a standardized marketable product has been satisfactorily worked out on a commercial scale in the treatment of by-product gypsum secured from the manufacture of phosphoric acid from either bone or rock phosphate of lime, and is the result

Fig. 1. Rock Gypsum from Nova Scotia
500 × Magnification

of two years of careful research work on the problem. During a portion of this time the recovery process was operated on a semi-commercial plant scale and the results of this work warranted the construction of a large commercial plant for the production of plaster of paris from this waste gypsum, with an additional plant for converting the plaster into plaster blocks; and these plants were completed and placed in successful operation in January, 1925.

The most serious problems encountered in converting this waste gypsum into a plaster of paris of standardized setting and strength

qualities were the elimination of the phosphoric acid left in the gypsum and the method by which the finely divided gypsum crystals or particles could be compacted or densified before the calcining treatment, in order that increased strength might be given to the calcined product.

As these two problems must be satisfactorily and efficiently overcome by anybody contemplating the recovery of synthetic gypsum waste from the manufacture of phosphoric acid, an explanation of the treatment involved is of interest.

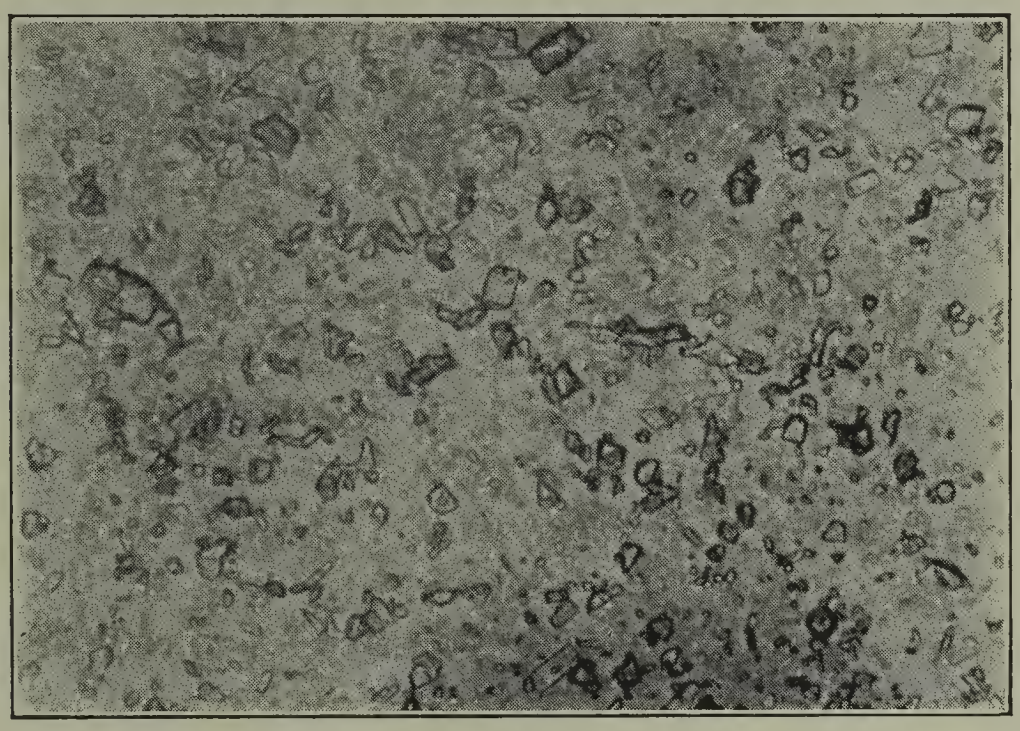


FIG. 2. Anhydrite from Centerville, Iowa
500 × Magnification

With regard to the effect of phosphoric acid on plaster of paris, it may be well to state that there are many crystalline and non-crystalline substances which will completely upset the hydration of plaster of paris. The ordinary plaster or stucco retarder is a vegetable or animal colloid, and when used in very small quantities serves to retard the crystallization of the plaster mixture so that a definite regulation or timing of the set of the plaster mass may be secured. Retardation of the set of plaster of paris is the universal practise for making it of commercial use, for without retarding and controlling the set of plaster, mortar made from it would set and harden so quickly that it could not be spread upon the wall. While stucco retarder answers this purpose, it must be used in small quantities. Even then the plaster mixtures in which it is used crystallize with reduced strength. The phenomenon noticed when

certain soluble salts or acids contaminate the plaster or gypsum from which the plaster is calcined is quite different, for while small quantities of many of these substances or salts retard the setting time and permit the satisfactory working of the plaster mass, there is no strength in the plaster so contaminated after drying out. Phosphoric acid, even in minute quantities, is one of the worst of such contamination products.

As to the density problem, it is a known fact that the more dense and compact plaster of paris makes the stronger setting crystal form. Commercial plaster of paris, as produced from the massive form of rock gypsum, is crushed, dried and pulverized to a fine powder before the calcining treatment, which in turn converts it into a heavy dense powder. Gypsums from some sections of the country are more dense and on this account make a more compact plaster powder which in turn is converted into a plaster of greater strength. Frequently plaster is ground in tube mills for the express purpose of increasing its density and strength. On the other hand, synthetic gypsum, due to its method of formation, is of considerable less density than is rock gypsum, and plaster of paris made from this synthetic gypsum forms a lighter, more porous plaster with consequent reduction in its ultimate strength on this account.

Detailed Steps in the Conversion Process

1. Pumping the precipitated gypsum, in slurry form, into Dorr thickeners which are used as storage for raw material supply.
2. Partial dewatering and washing of the gypsum slurry by passing over a continuous rotary filter.
3. Repulping the filter cake and neutralizing the free phosphoric acid contained therein by stirring in agitator tanks.
4. Dewatering and densifying the gypsum magma so treated by centrifugation.
5. Calcining the semi-dried, purified and densified gypsum into stucco or plaster of paris.
6. Converting this stucco into neat plaster mixtures, sanded plaster mixtures, plaster block or plaster board.

The Operation of the Process

All waste gypsum from phosphoric acid manufacture contains varying, but usually small amounts of free, as well as partially com-

All microphotographs taken at 500 × magnification

Fig. 3. Synthetic Gypsum from Phosphoric Acid Manufacture—Before Densification.

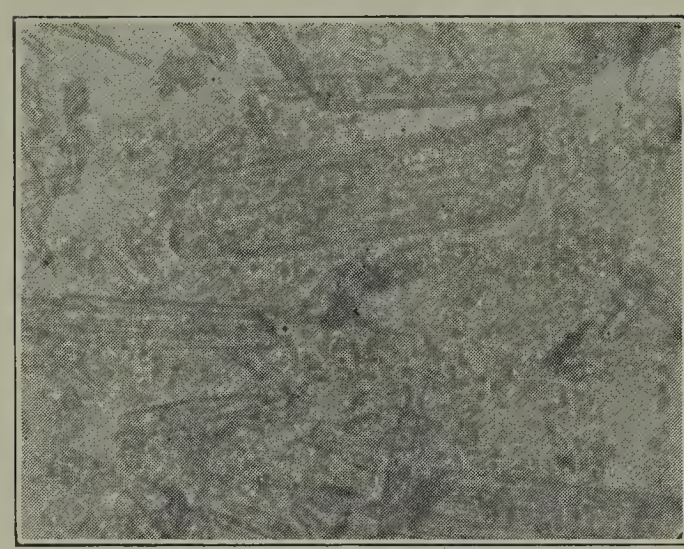


Fig. 4. Synthetic Gypsum from Phosphoric Acid Manufacture—Before Densification.

Fig. 5. Same as Figs. 3 and 4 but Taken After Densification Treatment.

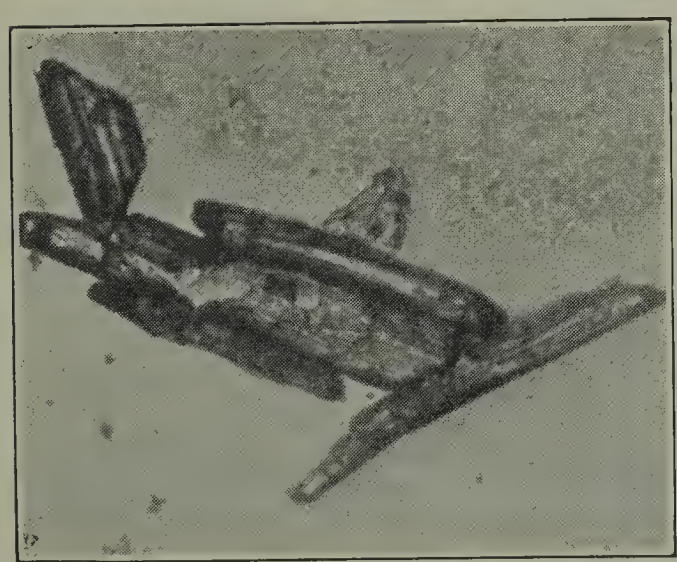


Fig. 6. Synthetic Gypsum After Densification Treatment Showing Compacting of Crystals.

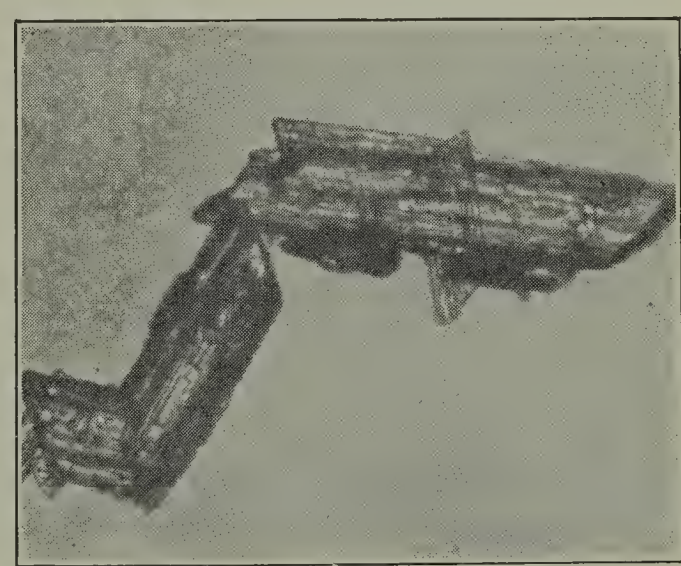


Fig. 7. Synthetic Gypsum After Densification Treatment. The "Twinning Action Due to Pressure Is Shown.

bined phosphoric acid. Washing alone will not serve to eliminate this acid or even reduce it to such an amount that it will not later appear in the calcined product, in at least a sufficient amount to cause erratic setting time and a weakened strength in the set plaster.

Probably the most obvious and cheapest neutralizing agent to be used for this purpose was hydrated lime. Unfortunately, however, calcium oxide or hydrate has a retarding as well as a marked weakening effect on plaster of paris manufactured from gypsum containing the lime salt, and on this account it could not be used. After experimenting with various salts which would combine with phosphoric acid to form a neutral or alkaline compound and at the same time fulfill the other requirements, it was found that neutralization with a water-soluble sodium salt—the carbonate or bicarbonate—gave the desired results in actually stabilizing and controlling the setting time of the plaster of paris made from gypsum so treated. This stabilizing action, or what is equivalent to a brief but definite staying of the initial set of plaster with a rapid completion of the final set, is of great value when plaster is to be used for making blocks, tile or boards, or in any work where rapid hardening action is desired. The ultimate strength of the plaster produced by this metathetical neutralization of the phosphoric acid with the sodium salt named above was in no way reduced by the treatment. Consequently the value of this treatment can be at once seen.

The application of the neutralizing agent occurs in the third step of the process outlined above; the calculated quantity of the sodium salt, as carbonate or bicarbonate, necessary to neutralize the phosphoric acid present being added to the gypsum magma in the repulper. Thorough agitation of the magma in contact with the neutralizing agent serves to produce the required chemical change throughout the gypsum mass.

The dewatering of the treated gypsum magma in the centrifugal machine (step four in process) brings about a definite physical change in the form of the gypsum crystal which is especially noticeable when gypsum having the needle form of crystal is so treated. To illustrate this fact a series of microphotographs were taken showing the crystal form of several types of synthetic gypsum before and after centrifugation. These indicate to a marked degree the influence centrifugal force exerts in bringing about the twinning or actual compacting of the individual gypsum crystals into larger crystal units.

In the later step of calcining this densified gypsum it was actually determined that plaster manufactured from all kinds of synthetic gypsum, which had been treated by centrifugal force before calcination, was of a more dense composition than plaster manufactured from the gypsum which had been dewatered by preliminary drying other than by the application of centrifugal force. This fact was demonstrated in actual practise by noting the increase in tensile and compressive strength of the densified gypsum plaster, which ran from 40 per cent in the needle form of crystal to 20 per cent in the finer more granular form of crystal.

With these two problems satisfactorily solved, the remaining steps of processing synthetic gypsum into plaster of paris on a large commercial scale were readily carried to completion by utilizing standard plaster manufacturing equipment.

Calcining Operation

In calcining natural rock gypsum the usual procedure in preparing the raw material involves its crushing, drying and pulverizing so that 95 per cent of the product will pass a 100-mesh sieve. In this finely divided condition the load on a plaster kettle in stirring this heavy mass of gypsum is considerable, and the power factor required for agitation during calcination is large.

In several localities in the United States a rather finely divided and generally impure form of weathered gypsum known as gypsite is used for plaster making, and the common practice is to collect this gypsite into plant storage and calcine it without preliminary drying. As the free moisture content of gypsite is a variable factor, running from 10 per cent to 25 per cent, depending on the season of the year in which it is gathered, considerable trouble is experienced in calcining it without preliminary drying. Kettles of large capacity are used and the time of calcination usually lasts from 5 to 6 hours as compared to a time of 2 to 3 hours for properly prepared and dried rock gypsum. Much trouble sometimes results from sticking of the moist gypsite charge on the bottom and sides of the kettles, and oftentimes calcining kettles handling gypsite are equipped with side as well as bottom scrapers.

In calcining synthetic gypsum trouble was naturally anticipated due to the rather high content of free moisture left in the gypsum after centrifugation. In the various gypsums treated this percentage of free moisture, after centrifugation, was found to vary from

15 per cent to 25 per cent. But the gypsum is discharged from the centrifugal machine in such an interstitially extended physical condition, due to the shaving action of the discharging knife blade upon the compacted gypsum mass within the machine, that sticking of the calcining kettle due to this moisture is entirely eliminated and no trouble has been experienced in directly calcining the gypsum in such condition, in from 3 to 4 hours, in the ordinary type of calcining kettle without the use of side scrapers.

The reason for this is attributed to the action of centrifugal force, which in the type of centrifugal used, that has a 60-inch basket and travels at 550 R.P.M., and will show an approximate peripheral speed of 8600 feet per minute. At this speed one pound of gypsum will exert a centrifugal force of 245 pounds at the periphery of the basket. This force serves to compact the gypsum crystal while the shaving action of the discharging knife of the machine, operated against the compacted gypsum mass in the machine, literally tears away the particles from the physically compacted gypsum mass and delivers them in an interstitially extended form; in which condition the free moisture content of these particles is so uniformly distributed that the discharged gypsum mass in such form cannot again be compacted at any ordinary physical pressure.

The manner in which a charge of this gypsum uniformly boils, from top to bottom, in the large calcining kettle when fed directly after discharging from the centrifugal machine, tends to show the non-compacting physical condition of this gypsum mass under calcining treatment. Again, the small amount of fuel required to actually drive off the free moisture and calcine a given unit of this gypsum into plaster of paris clearly demonstrates the free boiling nature of synthetic gypsum which has been prepared in the above manner. The calcining operation is under control conditions, recording thermometers being used, which show the exact time and temperature at which each charge has boiled to the first settling point and when each is ready for drawing off.

These conclusions have been reached as the result of treating several typical synthetic gypsums on a plant scale, in some instances amounting to 20-ton lots, so that it has been possible to compare synthetic gypsum produced from Tennessee, Florida and Kentucky rock phosphate with bone phosphate gypsum; as well as two distinct types of precipitated gypsum obtained as a residue from neutraliza-

tion of solutions containing sulphuric acid. The practical results secured from all of these commercial tests serve as proof to substantiate the claims made in the foregoing statements.

Present Conditions of the U. S. Gypsum Industry as Shown in Geological Survey Report

Before taking up the matter of manufacturing and plant costs it might be of interest to give a few figures on the production of natural rock gypsum as well as to point out the various uses for the crude and calcined product. The figures on production of gypsum since 1918 were taken from the United States Geological Survey reports and follow:

Gypsum Produced and Sold in the U. S., 1918–1923

Year	Crude Produced (Short Tons)	Value of Crude and Calcined Sold
1918	2,057,015	$11,470,854
1919	2,420,163	15,727,907
1920	3,129,142	24,533,065
1921	2,890,784	23,700,290
1922	3,779,949	29,361,151
1923	4,753,448	34,888,155
1924	5,042,629	42,724,507

In 1923 for the first time the quantity of gypsum mined in the United States exceeded 4,000,000 short tons, with an additional amount of 446,790 short tons imported from Canada, most of which was converted into plaster in the United States where it was sold.

Of the total tonnage produced in the United States in 1924 959,806 tons were consumed in the raw state by the manufacturers of Portland cement, while over 3,500,000 tons was converted into neat, sanded or fibre wall plaster. There was a total amount of almost 4,000,000 tons of gypsum wall plaster produced and consumed in the United States during 1924, with very close to 400,000 tons of neat plaster or stucco converted into plaster blocks, tile and plaster board.

Production Areas are Scattered

The production of gypsum in the United States comes from eighteen states, only four of which are located east of the Mississippi River, in which territory the consumption of gypsum products is

approximately two thirds of the total production. The state of New York is by far the largest producer of gypsum, followed by Iowa, Michigan and Ohio. In the southern states Virginia is the only locality wherein gypsum is produced, and as it is in these states where the larger percentage of synthetic gypsum is produced, an added impetus to the conversion and utilization of this form of gypsum should result because of this situation.

The steady increase in the demand for gypsum products in the United States can be attributed to the general use of plaster and products manufactured from plaster in all types of construction work. In addition to the quick hardening, easy working and fast drying properties of gypsum plaster, which properties insure speed in construction work, it is also fireproof and its use as an insulating material is of the greatest importance. Products manufactured from gypsum, such as poured gypsum floors and roofs, gypsum, concrete, plaster partition blocks and plaster board, are being used in ever increasing quantities throughout the United States, because they offer high resistance to heat, cold and sound at low cost per given unit of construction. This property, inherent in gypsum and the products manufactured from gypsum, forms a basis of great potential value for its future use in all kinds of construction work.

Plant Equipment and Manufacturing Costs

A modern gypsum manufacturing plant having a capacity of 80 tons per day of twenty-four hours of calcined plaster or stucco, erected and placed in operation under existing prices for machinery, equipment and construction work, will cost approximately $100,000. Such a plant is designed to take rock gypsum, crushed through 2-inch ring, and process it into the finished stucco in storage bins.

A plant of this size operated continuously with power costing 2 cents kw. hr., fuel (coal) for calcining at $5.50 per ton, common labor at 50 cents per hour, and handling gypsum costing $1.50 per ton delivered at the plant, should be able to convert it into calcined plaster or stucco in storage bins at a mill cost of $5.00 per ton, which does not include depreciation or overhead. Adding 15 per cent of this mill cost, which would be a fair allowance to cover depreciation and overhead charges, gives a total cost of $5.75 per ton for stucco produced.

On larger operations including 500 tons or more per day, the

cost allowance of $1.50 per ton of gypsum quarried or mined and delivered to the plant can be somewhat reduced, while the mill costs of operation are likewise reduced; so that with mining or quarrying and transportation costs of gypsum to the mill not exceeding $1.25 per ton, calcined plaster or stucco can be manufactured at a mill cost of $4.50 per ton, and adding 15 per cent of this mill cost for depreciation and overhead, gives a total cost of $5.18 per ton for stucco at the plant.

A plant for the recovery of synthetic gypsum having a capacity of 80 tons of finished plaster or stucco per day of twenty-four hours would cost approximately $80,000, and under similar operating conditions for power, labor and fuel for calcining and processing waste gypsum as sent to the dump, would produce calcined plaster or stucco in the bins at a total cost not exceeding $3.75 per ton. This figure covers depreciation and overhead charges.

In arriving at this cost figure actual costs of operating the recovery plant, as described in the first part of this paper, were taken as the basis for figuring the costs arrived at in the larger capacity plant, and these figures are given as follows.

Cost Analysis

Operating costs of producing 15 to 20 tons of calcined plaster (stucco) per day of 12 hours, including preliminary processing of by-product gypsum from phosphoric acid manufacture:

Precipitated Gypsum taken at no cost

Precipitated gypsum taken at no cost	
Labor at 50 cents per hour	$17.55
Electrical power at 2 cents per kw. hr.	14.25
Fuel, oil at $2.30 per barrel (14 gallons per ton stucco)	11.93
Supplies, chemicals and water	5.50
Repairs: Labor and materials	4.00
Overhead: Including taxes, insurance, supervision, office, heat and light	6.00
Depreciation:—7 per cent on cost of plant, —2 per cent on cost of building	7.50
Cost on 15½ tons stucco	$66.73
Cost per ton of calcined stucco	$ 4.30

The obvious direct saving in the per ton cost of processing synthetic gypsum as compared to manufacturing plaster from rock gypsum is in the preparation of the raw material. In the one

operation the work of crushing and placing the raw material (precipitated gypsum) in a finely divided physical condition has already been accomplished, as the result of the prior process which has produced it as a by-product. In the other operation rock gypsum must be quarried or mined, transported, crushed, dried and pulverized before it is reduced to the same physical condition as the synthetic gypsum, and the cost of doing this work even on a large scale is very close to $2.50 per ton of raw gypsum treated. In the manufacture of plaster or stucco from synthetic gypsum no cost for quarrying or mining, crushing and pulverizing is required. There is, however, a certain cost for chemical and mechanical treatment of this synthetic gypsum in order that it may be placed in a suitable condition for calcining into stucco, but this cost even on the small operating scale of 20 tons per day is actually less than $1.00 per ton of gypsum treated.

Also, in every plant having the handling and disposal of gypsum waste to deal with, there must be a certain charge made for this purpose. If such gypsum is converted into stucco, this charge, if not directly credited to the conversion process, will show up to reduce the cost of other products, which is an advantage, and while not actually figured in this estimate of costs must be considered a tangible asset nevertheless.

Consequently, a plant for the production of plaster or stucco from synthetic gypsum having a minimum capacity of 20 tons per day, located in the southern territory of the United States, would, if operated continuously, produce plaster or stucco at lower cost than any plant producing plaster from rock gypsum, with the added advantage of being within closer freight haul to the markets of consumption in this territory. As to what finished products such a plant could manufacture from this stucco would depend to considerable extent on the color of the plaster manufactured, its plasticity, strength and sand carrying capacities. Under certain conditions plaster block or plaster board might prove more attractive on account of off-color plaster, market conditions and earning standpoint. In the plant which has been referred to, after careful consideration, it was decided to manufacture plaster blocks primarily, because the plaster produced from the synthetic gypsum at this plant was badly contaminated with carbon, forming a gray plaster. But color in a plaster block makes no difference in its quality or sales value, as the blocks are invariably plastered upon after erec-

tion, so that plaster blocks made from this off-color and impure gypsum command the same sales price per square foot as when the color is white. On this account, a block manufacturing process was installed and is being operated in conjunction with the calcining plant.

Profits

The net profits to be expected in the operation of a plant for the conversion of synthetic gypsum into plaster or stucco, and thence into neat or fibred wall plaster or some other form of manufactured product, depend upon the size of operation and quality of plaster which can be produced. Even the recovery of as small a tonnage as 10 to 12 tons per day of a white, fairly pure precipitated gypsum would pay a large percentage profit on the investment, as such a product when converted into finishing or gauging plaster would show in some localities a profit of $10 to $12 per ton, with a minimum profit of $5 to $6 per ton when sold as neat or fibred wall plaster. On operations that would produce from 20 to 30 tons per day of good quality calcined plaster which could be converted into neat or fibred wall plaster, even if it were off-color, due to impurities in the rock phosphate, a fair profit estimate in direct competition with plasters manufactured from natural rock gypsum would be $5 per ton, but such a plant located in territory considerable distances from the rock gypsum producers would show a larger net profit than $5 per ton, and in some cases would be as high as $7 to $8 per ton.

If a plaster board or plaster block were considered the best form of ultimate conversion of the plaster, then a larger profit could be expected; and this profit figured on a per ton basis of calcined stucco or plaster should equal $8 to $9 per ton for blocks and $12 per ton for plaster boards.

The block department of the plant referred to in this paper has a capacity per ten hour shift of 3,600 square feet of 2-inch and 3-inch blocks. The type of block manufactured is reinforced throughout its length during the pouring of this stucco with a shredded rattan fibre, and is cast in 70-foot rubber molding belts having a tongue and groove side. The reinforced monolothic plaster slab thus formed in these belts is run off and sawed into blocks of standard 30-inch lengths. The blocks are then placed on cars and run through tunnel dryers where they are cured by elimination of the free moisture contained in them.

The average cost of blocks manufactured in this plant in a proportion of one third of the output as 2-inch and two thirds of the output as 3-inch blocks is 5 cents per square foot, and the average selling price for 2-inch and 3-inch blocks in the New England territory is 9 cents to 12 cents per square foot. The advantages of manufacturing a plaster block of this solid reinforced type are as follows:

1. Much less breakage in handling during shipment and on the job.
2. A plaster block made from synthetic gypsum treated in this manner affords better insulation than the hollow block of same thickness. It is 50 per cent stronger due to reinforcement while the weight of the block is approximately the same as the hollow block made from rock gypsum plaster.
3. The tongue and groove feature affords a stronger wall of better alignment at less cost for labor and mortar used in erection.
4. Blocks of this type can be laid without mortar as their type of construction permits the use of nails in tying the blocks together.

Conclusions

The operation of this process as applied to the recovery of synthetic gypsum should overcome the serious problems involved in the storage of large accumulations of gypsum waste resulting from the manufacture of soluble phosphates, especially where such plants are limited as to storage capacity or are too close to the large centers of population to permit of any room for storing the waste, or in handling except by loading on cars and freighting away. For plants confronted with such conditions the recovery of their waste gypsum output would answer a long-sought-for solution of the matter.

In general any successful effort for the recovery and conversion of a by-product into an useful article of manufacture reduces waste in industry, while more specifically the recovery of synthetic gypsum from the manufacture of acid phosphate would not only show great financial returns to the manufacturer of acid phosphate, but should at the same time reduce the price of fertilizer to the farmer.

Discussion

A Member: I would like to ask Mr. Edwards if he has had any experience with hydraulic pressure.

MR. EDWARDS: We have found that by submitting the gypsum to pressure it would bring about this simple cohesion. It is a matter of coalescence, to make the crystals join and change of solubility under pressure. There are various ways of doing it, but the commercial problem is to produce a machine which turns out large quantities with small power and labor cost.

PRESIDENT REESE: What is the time limit in that change?

MR. EDWARDS: It is probably very fast. We deliver a charge in three minutes. We operate the machine in the neighborhood of 20 minutes. It has been difficult to determine exactly the time limit in that machine, but in my opinion it comes within the first five minutes. As soon as the water or free moisture has been eliminated, the change in solubility under pressure takes place.

PRESIDENT REESE: Is there any temperature rise or fall in that change?

MR. EDWARDS: We deliver the material or magma to the machine at a temperature of approximately 150 degrees Fahrenheit, but after remaining in the machine for the period of treatment [viz. 20 minutes] there is naturally a considerable temperature drop due to radiation; but whether there is any exothermic or endothermic temperature change has not been determined.

A. H. WHITE (Ann Arbor, Michigan): It is an interesting thing that Mr. Edwards has been able to overcome the difficulties he mentions. But I wonder if he has been able to overcome other difficulties which have prevented the extensive use of gypsum in other fields. The heating or insulating value of gypsum has been well known. An effort has been made to use gypsum roofs over paper mills but there have been some failures reported on account of cracks appearing in the gypsum. It seems quite clear that part of the trouble is due to the hydration or dehydration of the gypsum after being put in place, on account of the exposure to the air. Do you know whether that difficulty has been met in the product that you put out?

MR. EDWARDS: The use of gypsum plaster for structural work in the past few years has come into great prominence, that is reinforced as a roof, or for floors. There are several bleacheries in this locality which have installed gypsum roofs. I was recently called to one of them which was having trouble along the line you speak of; but I rather think that the temperature even in a bleachery with the hot steam ascending, would be insufficient to dehydrate to such

an extent as to cause cracking. It could be caused by the softening of the gypsum, which could be readily overcome by waterproofing, using a suitable waterproof paint or wash on a gypsum surface. Possibly the cracking might be due to faulty reinforcement, but I think that in a great measure it has been overcome, although not entirely overcome.

PROFESSOR WHITE: Do you know of any gypsum roofs two years old now that have not had that trouble? I mean with continued heat and moisture?

MR. EDWARDS: Do you mean poured or pre-cast?

PROFESSOR WHITE: Poured.

MR. EDWARDS: Personally I do not know of any, but the president of the structural Gypsum Corporation in New York, Mr. Williams, was recently at our plant and they have put in hundreds of them, mostly of the pre-cast type, and some of those roofs have been in for 10 or 15 years. I cannot tell you from experience of the cast type, but I am sure there are many such as Mr. Williams spoke of.

DR. MAXIMILIAN TOCH: The pre-cast floor used is generally gypsum, but the gypsum ceiling is generally half lime.

PROFESSOR WHITE: We are talking about pre-cast roofs.

MR. EDWARDS: Yes, we are talking about 100 per cent gypsum.

MR. A. O. BOURNE, JR. (Patent Solicitor, New York City): Have you considered the merits of coverings—covering with rubber compared with covering with gypsum? Copper wire is covered with rubber, and I think there is a field for gypsum in that respect. I would like your views on the comparison of these two.

MR. EDWARDS: Of course rubber is an organic material, subject to decomposition and decay in time. It is also subject to change in consistency due to rise in temperature. Gypsum of course is a mineral and not subject to similar decay as organic products are. But I cannot see how they will cover copper wire with gypsum plaster and make it adhere. At the present time there is a wire on the market covered by a composition of asbestos which has the binding to hold it. If you can make gypsum stick to copper wire, I think it would be the finest insulating material in the world, but it would have to be water-proofed.

REFRACTORIES

By M. C. BOOZE

Read at the Pittsburgh Meeting, December 6, 1924

The question of suitable refractories for industrial furnaces is being given serious consideration to-day more than ever before and investigations on this subject are becoming rather common. The increased interest is due largely to the fact that the conditions of service in many furnaces have increased sufficiently in their severity to decrease to a marked extent the life of the material ordinarily used. This shortening of life is often attributed by the consumers to the fact that the refractories now on the market are inferior to those produced in previous years. When it is considered that the business is highly competitive, that the past consumption has not greatly reduced the raw material supply, and that methods are now in use for control of the quality of the product which were not thought of in the past, it must be realized that such an assumption is, except in isolated cases, erroneous.

Some of the underlying causes for the shorter life are the driving of the furnaces to increase capacity; shorter cycles of operation, entailing getting the furnace into production quickly and cooling rapidly when shut down; larger furnaces; reluctance to shut down and make necessary repairs to the linings, which throws a greater burden on the parts remaining; an increased use of low-grade coal; and improper construction due to the high cost of labor and inability to get men who will lay up the linings properly.

Of all the causes enumerated, the increased temperature is undoubtedly responsible for the greatest number of failures. While this is seldom evidenced in fusion or sufficient melting to allow the brick to run, it increases enormously the rate of attack by slag, the amount of vitrification and susceptibility to spalling, and the amount of deformation in the parts supporting an appreciable load. With some products the higher temperature will also result in an appreciable amount of shrinkage, opening cracks in the wall, which accelerate failure.

The steaming capacity of a boiler, the melting time in a metal-

lurgical furnace, the amount of glass taken out of a tank furnace—these are all affected to a very great degree by the temperature of operation. An increase of a comparatively few degrees makes possible a much greater output and consequently the refractories are used to the limit of their endurance.

The cry is naturally for a product capable of carrying this increased burden, one that will have at least the usual length of life when used under the more severe conditions. It was for the purpose of discussing the possibilities along this line that this paper was written.

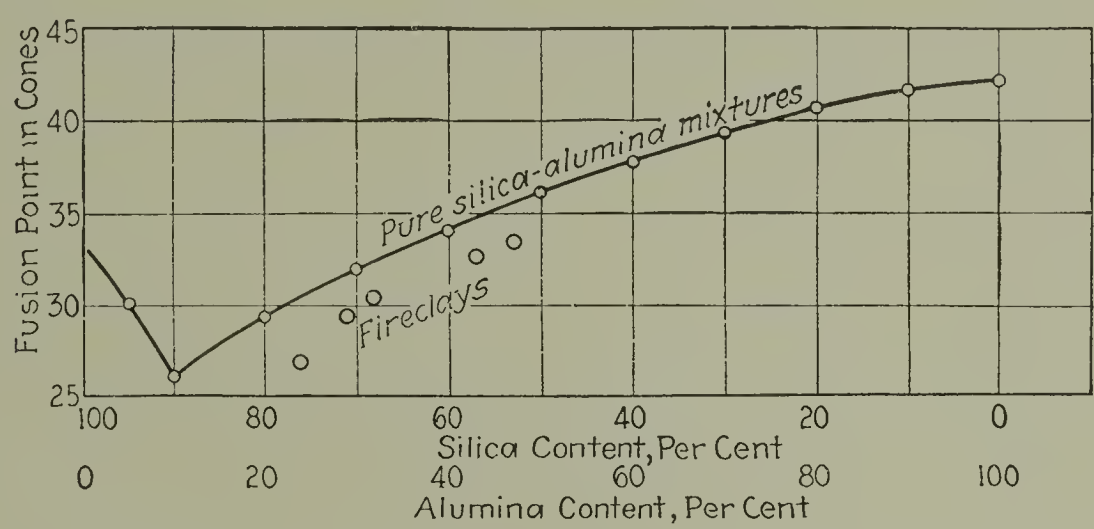
Consideration is given only to the products made from silica and from various combinations of silica and alumina, since these comprise the major portion of all refractories consumed. It is true that chrome, magnesite, silicon carbide, fused alumina, etc., are almost indispensable in the industries, but their use is greatly limited, due in some cases to the high price and in others to peculiar physical or chemical properties. Some developments may be expected with these latter materials leading toward extended use, but the developments will probably be in the method of application rather than in the products themselves.

In considering the subject of higher quality refractories, and in order to understand what would be involved in their production, it is necessary to have a general idea of the raw materials and manufacturing method used. The products made from fireclay will be considered first, as they are the most widely used.

The principal producing districts in the middle west and eastern part of the country are Pennsylvania, Missouri, Kentucky and southern Ohio, New Jersey and Maryland. Some of these districts are characterized by materials of peculiar composition, but on the whole the differences are more physical than chemical and even these are not sufficient to affect to a marked extent the service rendered, provided, of course, the usual care is taken in selection of the raw materials used and in the manufacturing processes. The variations in composition are not large. In some cases the difference is largely in the free silica content, in others the iron content or the percentage of total fluxes is the distinguishing item. The excess silica and fluxes are, of course, impurities, and lower the refractories of the product. In the accompanying diagram the fusion points of some fireclays have been plotted and a curve is also given, showing the melting points of various mixtures of chemically pure silica and alumina.

In each case the fireclays soften about two cones or approximately 40 deg. C. below the theoretical temperature for mixtures containing pure alumina and silica in the same proportions as exist in the corresponding clays. These reductions are due to the presence of such fluxes as Fe_2O_3, CaO, MgO, TiO_2, Na_2O and K_2O present in the clay as pyrite, siderite, magnetite, magnesite, anorthite, rutile, ilmenite, albite, orthoclase, etc. Their partial removal is possible by weathering, by low-temperature calcination and leaching with acid, and by washing.

In the case of flint clays, however (and it must be understood that the flint clays are as a rule very much superior to the plastic clays and make up about 80 per cent by weight of the clays used in the majority of fireclay brick), weathering or washing has little effect, due to the fact that the lumps are not disintegrated by water.



Comparison of Fusion Points of Pure Silica-Alumina Mixtures With Those of Fireclays. The Consistent Increment is Interesting

Even such a simple process as washing and settling out the relatively heavy and coarse accessory minerals is expensive and adds considerably to the cost of the product. Approximately 4 tons of raw clay goes into each thousand brick, which at the present time sell at about $40. Since the tonnage is large, washing would add considerably to the cost, entailing as it does grinding, blunging with water, settling, filter pressing, drying and recrushing. Weathering would remove some of the iron which was present originally as the sulphide and possibly break down some of the feldspars and remove a portion of the alkalis, but the process is slow, requiring storage for a year or more with frequent turning, and the improvement is but slight. By using plastic clay having a fusion point of cone 28–29 and flint clay fusing at cone 33 in the proportions of

1 to 4, fireclay brick are produced which fuse at a minimum of cone 32. Using plastic clay with a fusion point of cone 30–31 and flint clay of the same refractoriness as before, the product will in nearly all cases have a fusion point of cone 32–33 or ½ cone above the less refractory mixture. This corresponds to an increase of about 10 deg. C. It is doubtful if washing or weathering would affect the refractoriness of the plastic clay by three cones, and even then the results would hardly justify the expense.

The statement is often made that a fireclay brick is no better than the poorest clay incorporated in it, and if this were true, a manufacturer could well afford to wash or weather his plastic clay. This holds, however, only when a high proportion of inferior clay is used and not in the majority of cases where the proportion of plastic clay is small.

The processes of manufacturing have an important bearing upon the action of the refractories in service. The fineness of grind, degree of pugging or tempering, method of molding, drying and burning are all important. All of the qualifications necessary in an ideal brick, however, are not affected favorably by changes in the manufacturing methods; fine grinding, molding a dense body and hard burning all increase the strength, reduce the amount of shrinkage in service and lower the amount of deformation under load, but each of the methods tends to produce a brittle material which will spall readily. While the manufacturers may be and usually are familiar with the effects produced by varying the manufacturing processes, they are ordinarily compelled to steer a middle course under the necessity of producing as nearly as possible an "all around" brick.

Disadvantages of Some Raw Materials

In the southeastern states, deposits of kaolin are found that are about as free from impurities as could be desired as far as refractoriness is concerned, the fusion point being about cone 35, or near the maximum limit for clays. This material is being used to some extent in refractories, but it has the disadvantage of being difficult to shrink completely on account of its high degree of purity and its fluffy nature. In one case it is being thoroughly calcined and then made into brick, but at such an expense that the product sells for $250 per thousand.

Numerous attempts have been made to manufacture refractories

from bauxite, but this material ceases shrinking only when it has become so brittle as to be very susceptible to spalling and its use has been practically discontinued.

Within the last few years brick made from diaspor have been placed on the market that are of high refractoriness and that have proved to be particularly well suited to certain service conditions. The diaspor, which is a monohydrate of alumina and which as found contains from 10 to 30 per cent of silica, occurs in a limited area at a considerable distance from railroads and is ordinarily found in lenses surrounded by clays of inferior refractoriness, so that the expense of mining it is large and products made from it necessarily command a high price.

It is possible that new and cheap sources of supply of such high-grade refractory materials as diaspor, sillimanite, andalusite, etc., will be discovered, but until they are we must look to the fireclay to furnish the bulk of our refractories and, as has been pointed out, no marked increase in quality can be expected in products made from these.

Silica brick are manufactured from quartzite and lime, the latter being added in small amounts to make the ground "mud" more easily molded, and the brick stronger in the dry and burned state. It also aids in the inversion of the quartz to the more desirable cristobalite and tridymite forms. This type of refractory is noted for its rigidity under load at temperatures even near its fusion point and its use is being extended, replacing fireclay brick in many continuously operated furnaces.

The Medina, Baraboo and Alabama quartzites, from which the bulk of the silica refractories is made, are quite similar in their chemical compositions, containing about $97\frac{1}{2}$ per cent SiO_2, $1\frac{1}{2}$ to 2 per cent Al_2O_3 and Fe_2O_3, and $\frac{1}{2}$ per cent lime, magnesia and alkalis.

The refractoriness is affected by the silica content, but the variations in the rock as selected for refractories are seldom sufficient to have a marked effect upon the fusion point. The strength of the burned brick is determined largely by the grind, the amount of glass present and by the crystal intergrowth. In burning, about 75 or 80 per cent of the quartz is inverted to cristobalite and tridymite with a considerable increase in volume. The amount of inversion is determined by the temperature and duration of the burn and by the action of the fluxes present, which apparently serve as catalyzers. The lime that is added aids in this inversion,

but if the rock used is too pure, inversion will proceed slowly and the strength will be low. The maximum silica content is apparently between 98 and 99 per cent for satisfactory brick.

It is desirable to produce a maximum of inversion during burning in order that the brick will not expand unduly in service. Since quartz has a specific gravity of 2.65, cristobalite 2.33 and tridymite 2.27, it is evident that complete expansion would be reached only when the quartz was all inverted to tridymite.

Variations Due to Kind of Silica

The three crystalline forms of silica named above exist in alpha and beta forms. In the cases of quartz and cristobalite, the change from alpha to beta is sharp and is accompanied by a considerable volume change. The transformation of cristobalite takes place at about 220 deg. C. and of quartz at about 575 deg. C. Because of these sharp and rather large volume changes, silica brick containing either of the two minerals in large percentages are apt to spall if heated or cooled rapidly over ranges including the temperatures given. While tridymite changes from the alpha to the beta form, the transformation is not sharp nor is the amount of volume change as great as with quartz and cristobalite and for that reason brick consisting largely of this crystalline form are not as susceptible to spalling as those in which the other forms predominate.

In the presence of a flux, quartz inverts slowly to tridymite at 870 deg. C., which, in turn, inverts to tridymite at 1,470 deg. C. Without a flux tridymite is not formed, the quartz going directly to cristobalite at 1,250 deg. C. In the case of silica brick, the fluxes are not sufficiently reactive to produce much tridymite, the quartz first changing to cristobalite, which then slowly goes to tridymite on continued heating either in a kiln or in use, provided the temperature is below 1,470 deg. C. An idea of the speed of tridymite formation can be obtained from a paper by J. Spotts McDowell entitled "A Study of the Silica Refractories." In this he shows that a brick of regular grind after one burn at cone 15 in a commercial kiln contained 26 per cent quartz, 4 per cent tridymite and 70 per cent cristobalite. After three burns it contained 16 per cent quartz, 19 per cent tridymite and 65 per cent cristobalite. If tridymite continued to be formed at this rate, he points out that ten burns would be required to produce 80 per cent. If the same

changes were accomplished in one burn, the kiln would have to be held at the maximum temperature for weeks with an extremely high coal consumption and considerable damage to the kiln. The spalling properties of the brick would probably be benefited to a noticeable extent by this long burning, but as the difference in specific gravity between cristobalite and tridymite is not large, the amount of increased expansion obtained would be relatively small.

Patents have been obtained covering the use of certain catalyzers that increase the rate of tridymite formation. When incorporated in the brick, the results have not been encouraging. It is also proposed to form the tridymite by the aid of one of these catalyzers before incorporation in the brick. This is also covered by patents, and while some improvement may be noted, the cost will, of course, be materially increased, due to the double burning required. It is not possible to say how much the improvement will be if there is any, since no brick of this type have appeared on the market, and consequently no general tests have been made.

In the case of both silica and fireclay refractories, only the items of major importance have been covered and an attempt has been made to show that in some cases efforts to produce a marked increase in quality would meet with little success and that in others the increase in cost would be out of proportion to the results obtained. There are, of course, other improvements possible than those mentioned, but they are considered to be of minor importance.

It is improbable that a refractory will be produced at a moderate cost that is decidedly superior to those now on the market. The improvements that may be looked for will be largely in greater uniformity—in the raw materials used, in the structure and burn, and in the size and shape.

Discussion

Mr. Moore (in the chair): May I ask what is being done to reduce the porosity of the brick to prevent breathing.

Mr. Booze: The fire clay brick?

Mr. Moore: Of course you have been referring more particularly to acid brick. A great demand comes on the basic brick rather than acid brick.

Mr. Booze: You mean magnesite brick?

Mr. Moore: Things of that kind. Experiments have shown that especially in the basic brick it is liable to breathe and slough

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off. Take for example where you have sublimed sodium sulphide in the atmosphere it will breathe and breathe again, and the brick will slough off. In certain experiments that we have carried out putting in dense brick without pores, the brick will go into the wall, and, subjected to the same conditions, the other brick will go off all around it and the less porous brick will stand out like a sore thumb.

Mr. Booze: We know that the strength and porosity of magnesite brick are affected to an appreciable extent by the burning treatment. The brick you refer to may not have been burned hard enough.

Mr. Moore: It isn't shrunk enough?

Mr. Booze: The magnesite used in the brick is ordinarily almost completely shrunk as indicated by its high specific gravity. The product made from this calcined magnesite, however, is subject to shrinkage due to pore spaces that are present when the brick are first manufactured. These pores are partially closed in burning due to softening of the material used.

Mr. Moore: By taking the brick as a whole, it is still porous?

Mr. Booze: Yes.

Mr. Moore: Even though it is a magnesite brick?

Mr. Booze: Yes, it is possible to obtain brick made from magnesia that has been fused in an electric furnace which are almost non-absorbent. These, however, are quite expensive and also spall more readily than the magnesite brick that are commonly used.

Mr. Moore: Is there any further discussion on this paper or any question to ask? I believe that is the last paper in the program. We will adjourn.

THE CONTROL OF FURNACE ATMOSPHERE

By W. TRINKS

Professor of Mechanical Engineering,
Carnegie Institute of Technology

Read and Discussed at the Pittsburgh Meeting, December 4, 1924

The design and operation of industrial furnaces present problems, the solution of which requires the services of more than one engineering profession. Many of the problems such as the effects of furnace atmosphere upon the material being heated are purely chemical, but their solution calls for the services of the metallurgist, the mechanical engineer, and the electrical engineer, as well as for those of the chemist.

In general, we differentiate between an oxidizing atmosphere and a reducing atmosphere, with the hair-trigger adjustment of the so-called neutral or indifferent atmosphere standing in between. By rights, we should also consider the effects of sulphurous gases in the products of combustion, but, as a rule, we pay no attention to their presence, although some mysterious actions in the finishing of the material can be traced to the presence of sulphur combinations in the furnace gases.

In the treatment of control of furnace atmosphere, we must distinguish between fuel-heated furnaces and electrically heated furnaces. The present paper deals principally with fuel-heated furnaces.

The effects of an oxidizing atmosphere are indicated by the name and need not be dwelt upon. Since industrial heating aims to impart heat only, without any chemical change, a perfectly neutral furnace atmosphere is very desirable. However, it is well known that an atmosphere consisting of nitrogen, carbon dioxide, and water vapor is not neutral at temperatures above a red heat, particularly in the presence of certain base metals. In a furnace, both carbon dioxide and water vapor dissociate to a much greater extent than laboratory tests would indicate. There are several reasons for this. Both gases exist in the furnace at low partial pressures, and it is known that dissociation is greater at low pressure than it is at atmospheric pressure. Furthermore, some of the

molecules in gases impinge upon each other at all times, dissociate, and immediately recombine if left to themselves. In the presence of an easily oxidized metal, dissociation still takes place, but recombination does not, because the oxygen goes to the metal, instead of returning to the carbon or hydrogen. If iron or steel is being heated, a great deal of oxidation is caused by water vapor, because the heat developed by the combination of unit weight of oxygen with iron is greater than that developed by combination with hydrogen.

Since neutral atmospheres cause oxidation, furnace heaters usually work with so-called reducing atmospheres. "Keep her smoky, boys!", is the slogan. The laws which connect temperature of metal and of furnace atmosphere, composition of gases, and rate of oxidation have not been found as yet; they may be known to a few eminent physical chemists, but the rank and file of furnace engineers know nothing about them. However, the fact that reducing atmospheres protect steel from excessive scaling is known. To what extent it pays to work with reducing atmospheres is a question of dollars and cents, because reducing atmospheres cause a loss of fuel. On account of the fact that hydrogen burns about $2\frac{1}{2}$ times as quickly as carbon monoxide, the latter is the unburnt constituent which is most commonly found in reducing atmospheres. The loss of heat which is caused by 1 per cent of carbon monoxide in the flue gases depends upon the nature of the fuel and upon the excess of air, but has an average value of 3 per cent. If two or three per cent of carbon monoxide in the products of combustion are necessary for protecting material such as steel from scaling, then a loss of 6 to 10 per cent of the heating value of the fuel must be taken into the bargain. The furnace engineer, for that reason, faces a dilemma. Perfect combustion with no loss of heat due to unconsumed fuel causes heavy loss by scaling. Protection of metal by a reducing atmosphere causes loss of heat due to unconsumed fuel. A brief calculation will be of assistance in driving home the importance of this problem. Let steel billets or forgings which cost $40 per ton be heated. Let the furnace loss be 2 per cent with a reducing flame, and 4 per cent with a slightly oxidizing flame. But 2 per cent of $40 equals 80 cents. Let 200 pounds of coal be used to heat a ton of steel, and let the coal cost $3 per short ton. Then the cost of the fuel for heating a ton of steel is 30 cents. It is at once evident that a slight difference in the furnace loss is of far

greater monetary influence than the whole fuel bill. This fact explains the peculiar condition which exists in many plants. Heaters try to work with strongly reducing atmospheres so as to save furnace loss, while fuel engineers try to adjust for neutral products of combustion.

With ordinary means, it is rather difficult to obtain the desired mildly reducing atmosphere which contains from 2 to 3 per cent carbon monoxide and is free from oxygen. The analysis of the flue gases may indicate the correct composition, and yet excessive scaling may take place due to poor mixing of air and fuel, and slow combustion. Stratification of gases, with delayed combustion, is often practiced for the purpose of equalizing temperature throughout the furnace, which is done by means of a long, lazy flame. Such a flame contains strata of fuel and of oxygen, which latter attacks the material being heated, if it has a chance to come in contact with it. To prevent oxidation, the fuel gas is frequently directed along the charge, while air is admitted on top of the gas under the roof, so that the charge is practically bathed in fuel gas, while the roof is supposed to be kept cool by the air.

No matter what the methods of combustion and of mixing of fuel and air may be, the maintaining of a constant furnace atmosphere with varying rates of fuel supply requires a constant fuel-to-air ratio. Of great assistance is constancy of furnace pressure, which can be obtained by adjustment of the vent damper or dampers. The latter are frequently not adjusted, and in other cases are absent. Automatic adjustment of a single damper is somewhat inconvenient, but, becomes impracticable if it is to be extended to many dampers, because complicated mechanism must be introduced. For that reason, automatic damper adjustment is seldom practiced. The vents are so adjusted by hand, that a slight furnace pressure exists with the lightest regular rate of heating. Increased rate of heating then results in greater furnace pressure, and in blowing of furnace gases out of the doors and peep holes.

The commonest method of adjusting furnace atmosphere consists in letting the eye of the heater decide whether the atmosphere is sufficiently reducing. With a few fuels, that decision is comparatively easy, because a reducing atmosphere is smoky and hazy, whereas a clear, transparent atmosphere is neutral or oxidizing. In this difference lies the reason why most heaters maintain smoky atmospheres in their furnaces. With a few fuels, such as coke oven

gas, blue water gas, or clean producer gas, it is practically impossible to judge the chemical character of the atmosphere by the eye. In this case, we must either depend upon a flue gas analysis or upon

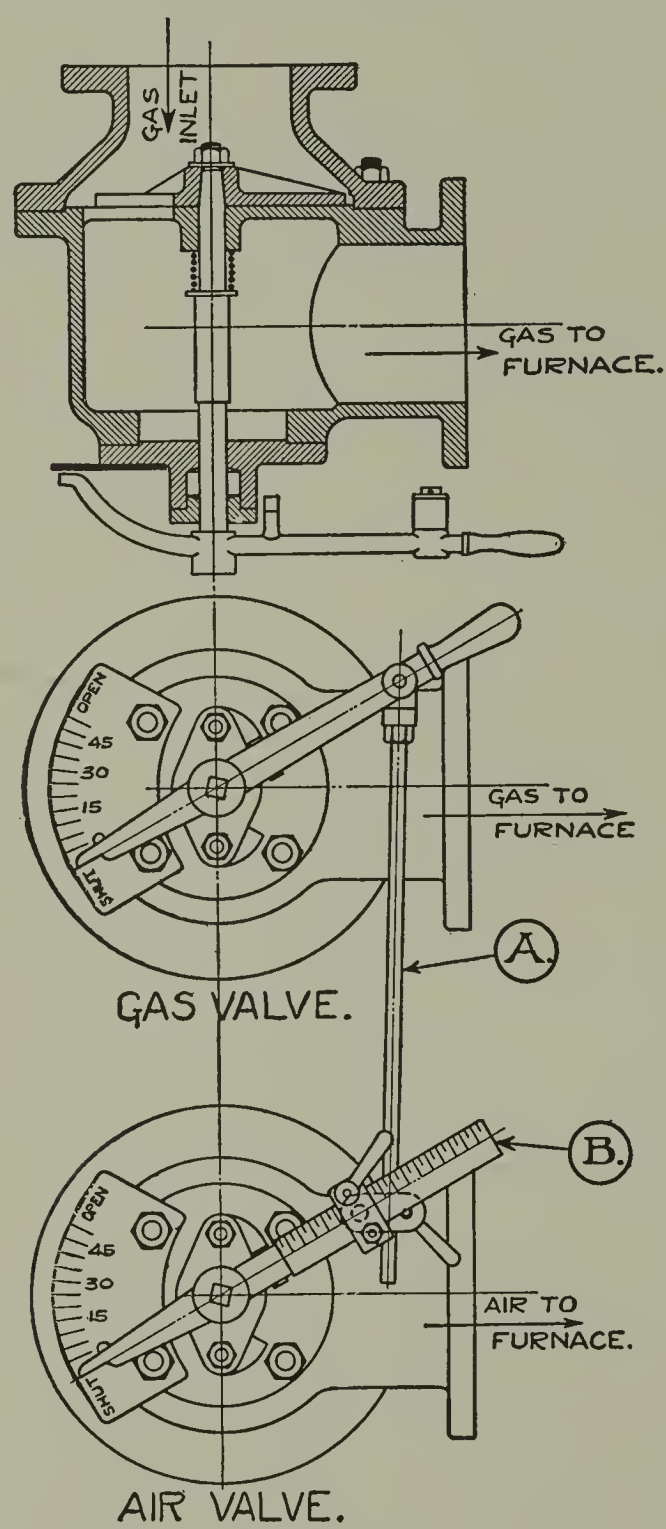

FIG. 1

automatic proportioning devices. It is rather unfortunate that, in spite of the progress of chemistry, no simple and reliable oxygen recorder has been invented; if such an indicator existed, the heater would adjust for no oxygen and then go just a little further in the same direction. However, there are now several comparatively simple electrical indicators on the market for showing combustible

matter in the products of combustion. For large furnaces and important work, their use is recommended.

It is a fortunate coincidence that correct and automatic proportioning of air and fuel is easiest with those fuels which offer the greatest difficulty to the eye of the heater with regard to judgement of character of furnace atmosphere, namely with gaseous fuels.

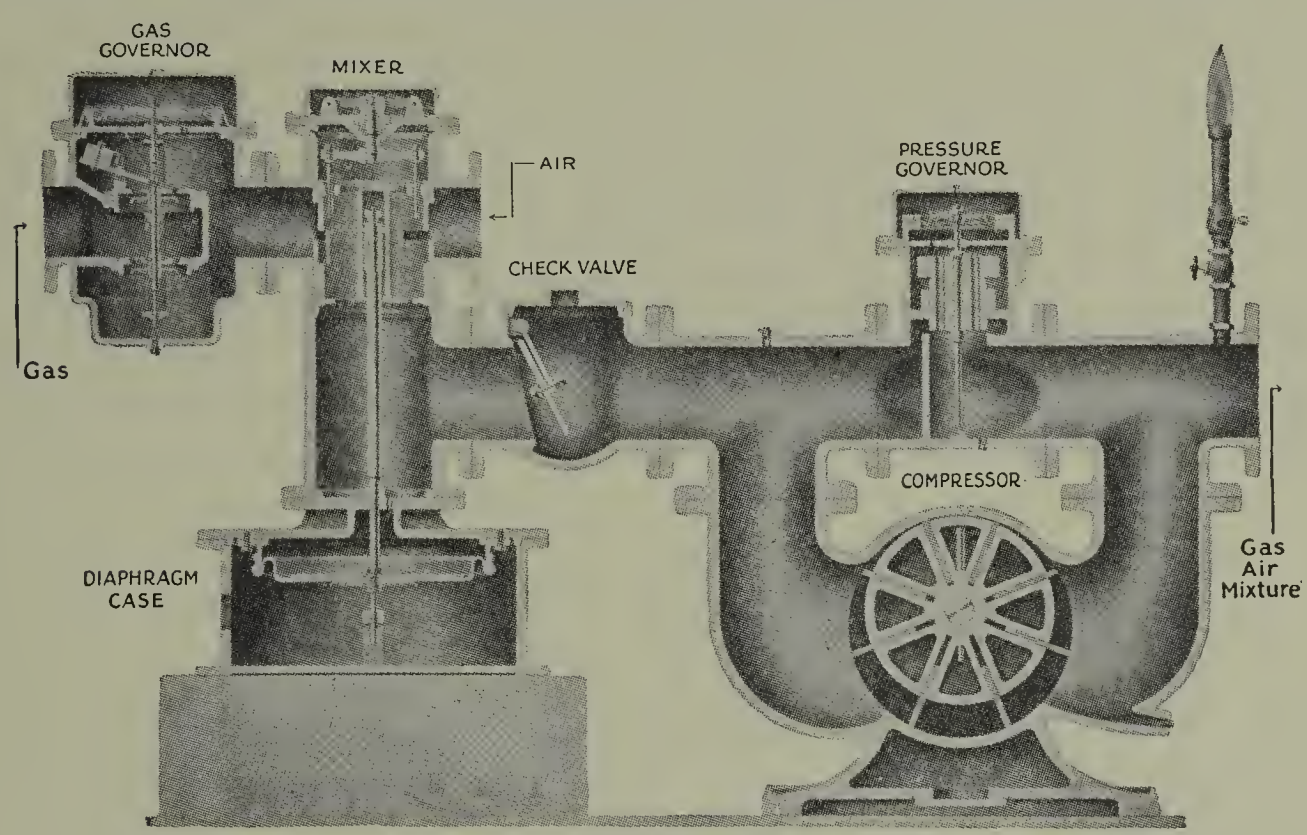

FIG. 2

With any fuel, the most natural and self-suggestive step towards control of furnace atmosphere consists in mechanical interconnection of fuel supply and of air supply. Interconnected valves for air and gas are shown in Fig. 1. Devices of this sort have been tried very often, and have been discarded in the great majority of their applications, because conditions which were necessary for their success were not provided. These conditions are: (1) Constant gas pressure, (2) Constant air pressure, (3) Constant gas quality, (4) Constant gas temperature, (5) Constant air temperature. Even small variations in these quantities are enough to upset the hair-trigger adjustment of correct fuel-to-air ratio. The heater disconnects the valves and goes back to hand adjustment, guided by the appearance of the furnace.

This feature has lately become of importance, because automatic temperature control apparatus is frequently designed with interconnected air and fuel valves, and because these devices are commonly

supposed to control not only furnace temperature, but also furnace atmosphere.

A more recent development for the purpose in question is that of proportional mixers. Several types of such mixers have been introduced. In most of them gas is reduced to atmospheric pressure by a reducing valve before it enters the mixer proper. Gas and air flow through a proportional mixing valve which is similar to that used on gas engines. The mixture is sucked through the valve by a fan, a jet, or a rotary blower and is delivered to the furnace by the pressure of these pumping devices. If the gas pressure regulator works well, both fuel and air are indeed taken in at constant and equal pressures. However, the condition of correct working of the pressure regulator is not easily fulfilled, if the gas contains traces of gumming or sticky substances. They cause the valve to stick, and interfere with regulation.

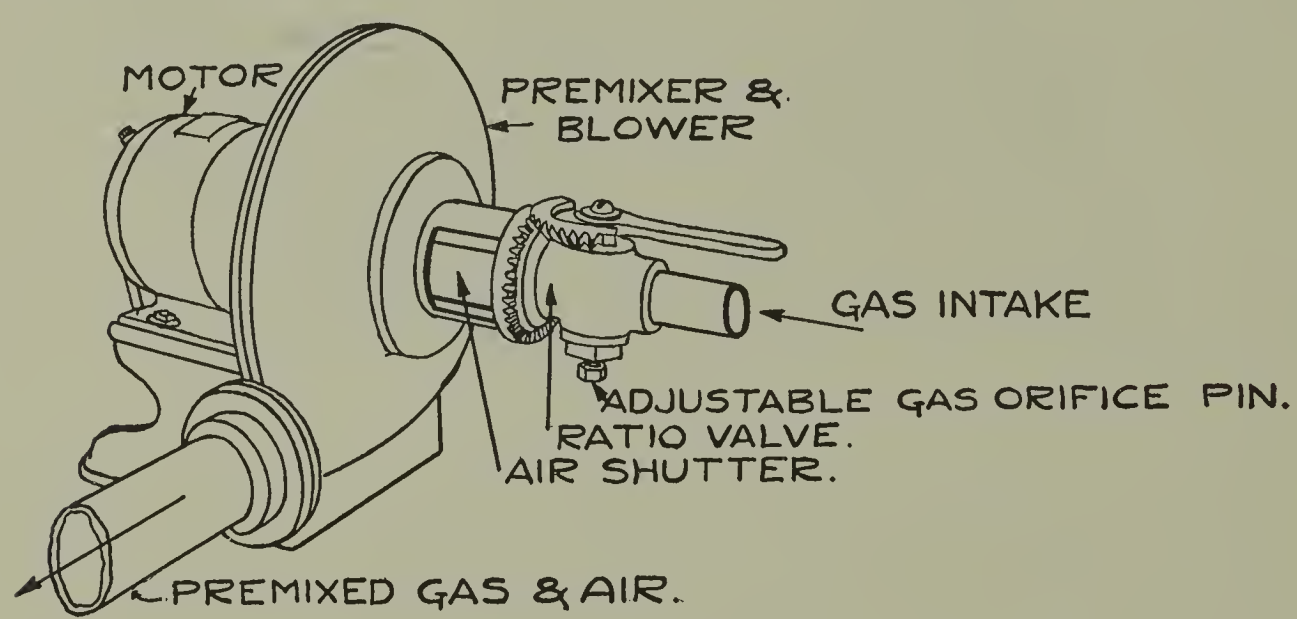

Fig. 3

Figs. 2, 3, and 4 show proportional mixers in which the moving of the mixture is obtained respectively by a positive blower, a fan, and a jet. If the rate of heating is low, and if the mixture of gas and air is almost correct for perfect combustion, back-firing occurs. In long pipe lines, this occurence means quite a disturbance in the operation, and sometimes damage to the equipment. For that reason, the mixture is quite often made too rich in fuel, and additional air is induced by the mixture passing through a nozzle at the furnace. This arrangement does away with the back-flares, but it also does away with the positiveness of atmosphere control. In the arrangement of Fig. 2, the induction of air at the furnace is openly

advocated by the builders of the equipment. With the arrangement of Fig. 3, it is not advocated, but is commonly practiced. With the arrangement of Fig. 4, it is not necessary, because the injecting jet and the mixing cone can be placed right against the furnace.

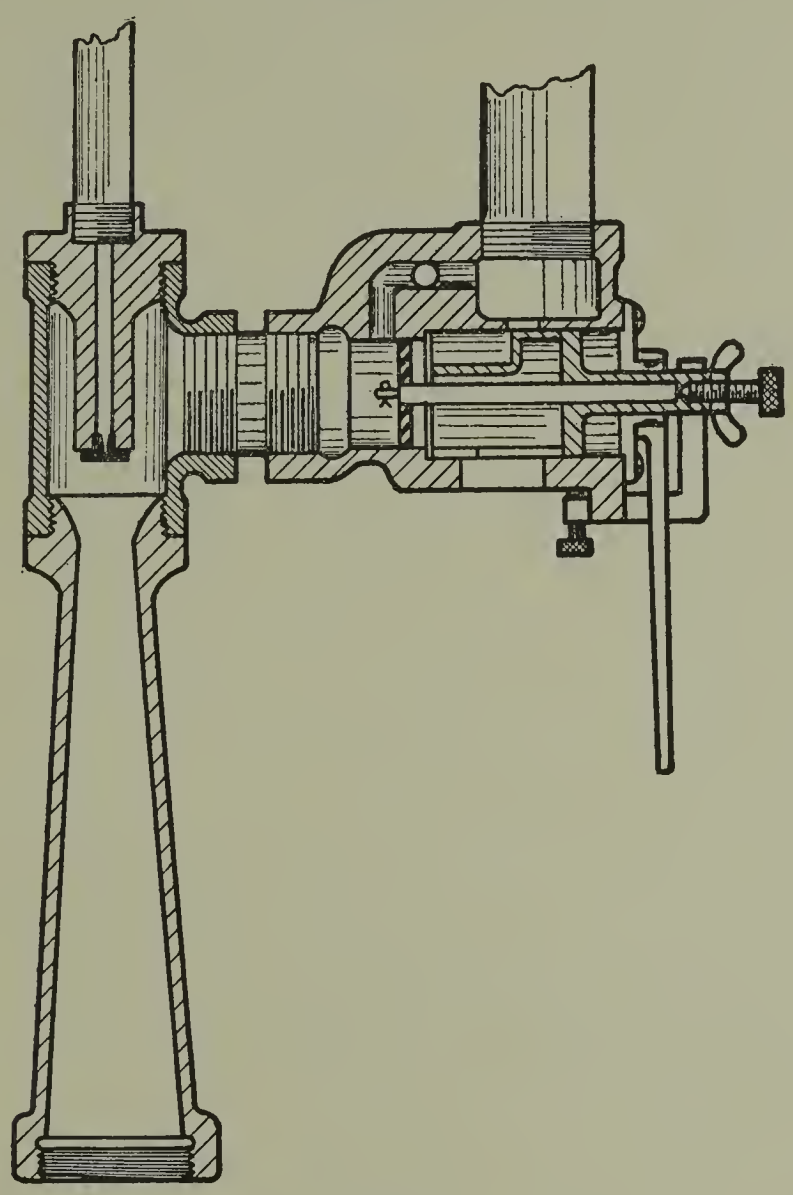

Fig. 4

Whenever the gas carries impurities which can clog a pressure regulator working with a small aperture, it is better to compress the gas and let it induce air. It has been found that by correct design of entraining nozzles the amount of entrained air is proportional to the weight of entraining gas over a remarkably wide range of turn-down. The apparatus is sensitive to variations in the back pressure, but with properly designed furnaces and burners, back pressure is a function of the quantity of the inducing fluid passing through the mixer in unit time, and can be compensated for in the design of the mixer. Several proportional mixers based upon this principle are on the market. A widely used design is shown in Fig. 5.

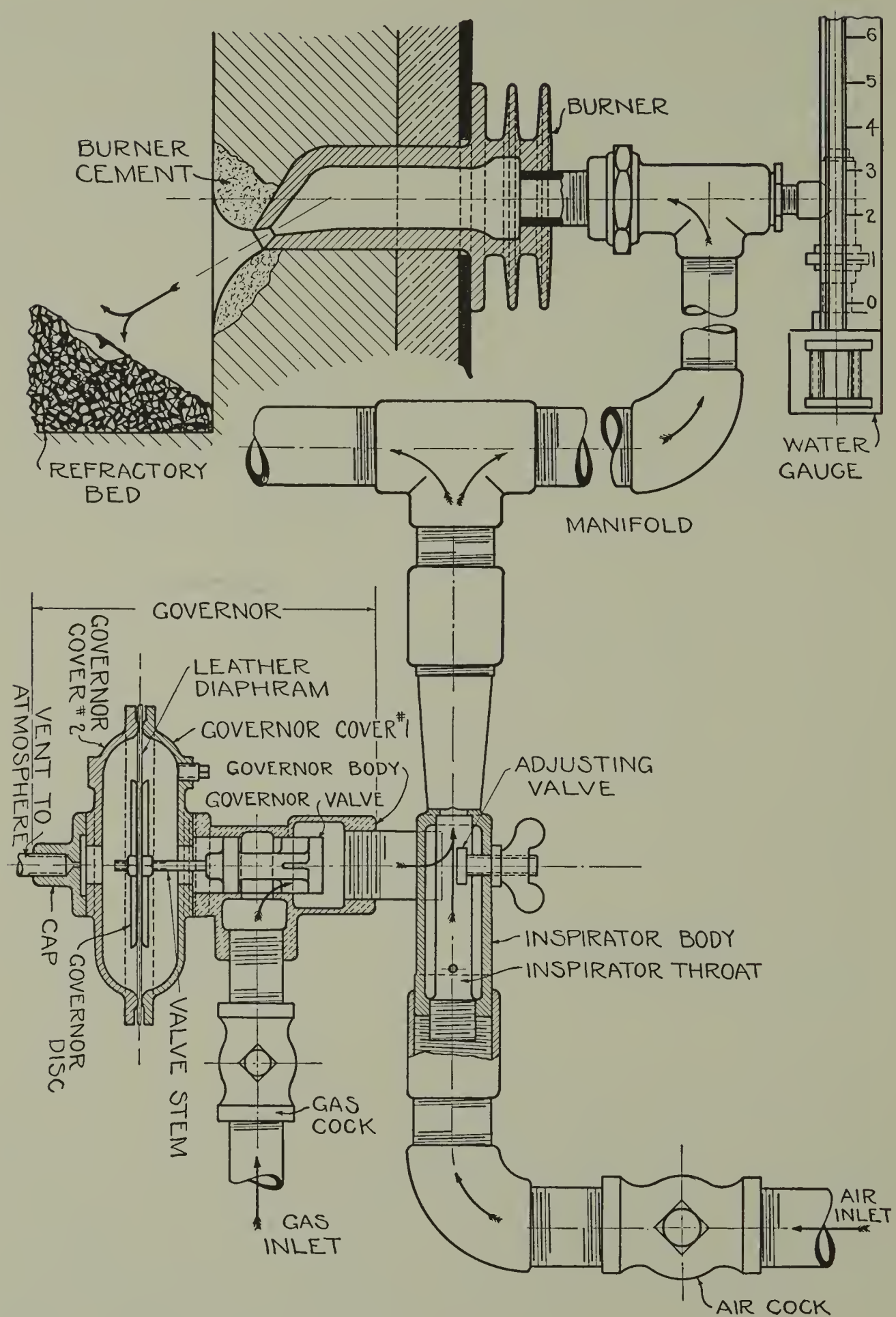
BURNER
BURNER CEMENT
REFRACTORY BED
WATER GAUGE
MANIFOLD
GOVERNOR
GOVERNOR COVER #2
VENT TO ATMOSPHERE
LEATHER DIAPHRAM
GOVERNOR COVER #1
GOVERNOR BODY
GOVERNOR VALVE
ADJUSTING VALVE
CAP
GOVERNOR DISC
VALVE STEM
INSPIRATOR BODY
INSPIRATOR THROAT
GAS COCK
GAS INLET
AIR INLET
AIR COCK

FIG. 5

In the proportional mixers under discussion, the ratio of air to gas remains remarkably constant over a wide range of turn-down, but, if a very wide range is required, variations in the ratio do occur. For the purpose of eliminating even small variations, a British engineer devised the trick shown in Fig. 6. He put into the

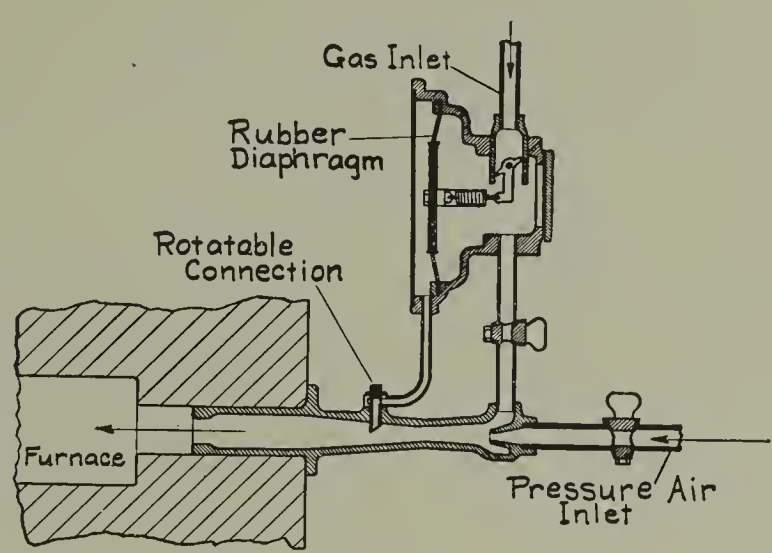

FIG. 6

injection tube a rotatable pipe, the lower end of which is cut on the diagonal. The static head and part of the dynamic head of the fluid passing through the expanding tube then act upon the gas regulator and vary the pressure with which the gas enters the outer section of the Venturi tube. By a part rotation of the inclined cut tube in the nozzle, the dynamic head can be adjusted, and the tendency to give too much gas at high rates of flow can be counteracted.

Still another, and quite different, principle has been used for the purpose of securing proportionality between gas and air flow at all rates of flow. It is illustrated diagramatically in Fig. 7. It is based on the fact that a fluid passing through an orifice produces a pressure drop which is practically proportional to the square of the velocity of flow provided the fuel has a low viscosity. In the illustration, air flows through the pipe shown at the left, while gas flows through the one shown on the right. Each pipe carries an orifice, and the pressure-drops through the two orifices, by acting on diaphragms or floats, produce forces which are pitted against each other. The orifices must be so selected that, with the correct ratio of gas to air, the forces caused by the pressure differences of the two orifices just counterbalance each other. If either more or less air than the correct amount flows in proportion to the gas, the forces

become unbalanced and a relay is set into motion. In the illustration, contact is made on one side or the other of a sensitive electric switch. By means of an electric relay, an electric motor is started in one or the other direction and turns a butterfly valve, thereby adjusting the air flow until the correct ratio of gas to air has again been obtained. The various parts are so clearly shown in the illustration that no further comment is necessary. The ratio of gas to air can be varied by changing the size of either one of the two

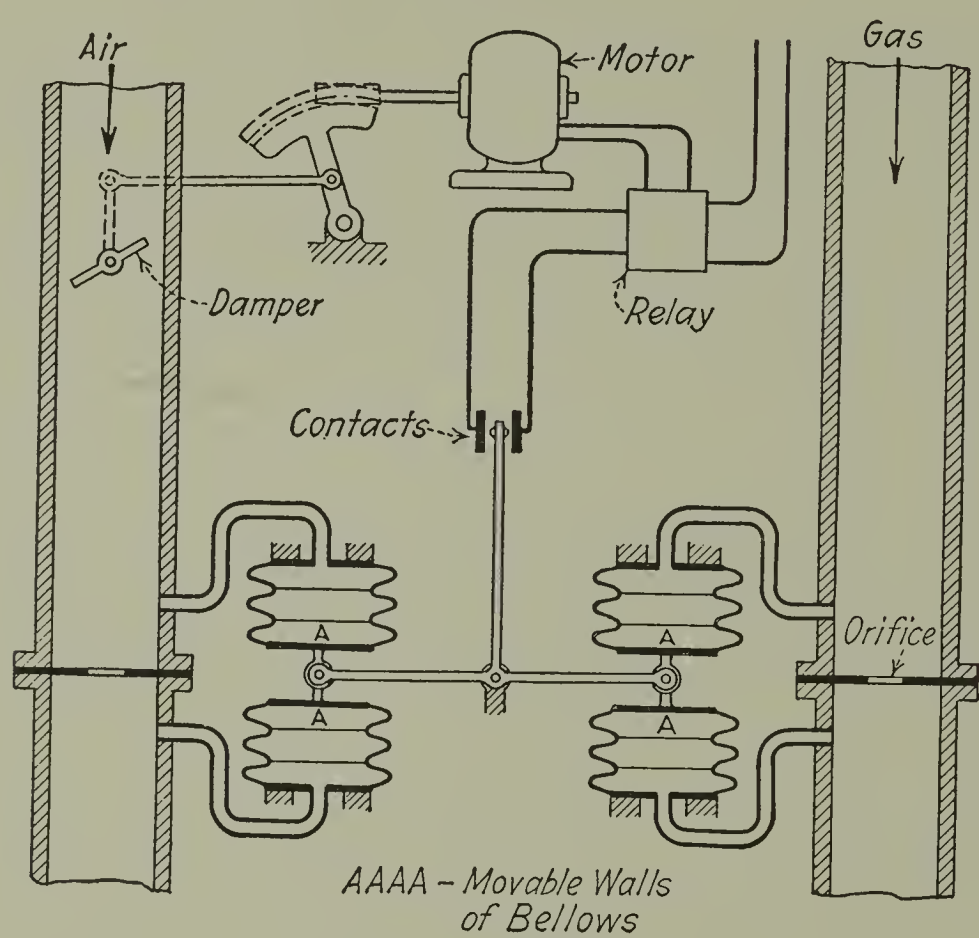

Fig. 7

orifice plates. If a variation or adjustment is to be obtained while the equipment is in operation, one of the orifices can be made adjustable, for instance by a slide which can be operated from the outside. Up to the present time, no means for automatic control of furnace atmosphere has been devised, if raw producer gas serves as fuel; soot and tar in the gas clog up any automatic control valve.

The problem of controlling furnace atmosphere, if the combustion air is preheated, is very far from a satisfactory solution. If the temperature of the preheated air could be maintained constant, independent of the rate of heat delivery to the furnace, the problem

would be no different from that which exists with cold combustion air, except that hot, explosive mixtures cannot be carried in pipes, on account of the greatly increased tendency to light back and explode. But a constant temperature of the preheated air cannot be guaranteed, except by complicated thermostatic control apparatus, which engineers are loath to apply. The first cost of such equipment is considerable, and its maintenance cost is high.

With liquid fuels, such as oil or tar, automatic control of furnace atmosphere is much more difficult than it is with clean, gaseous fuels. The simplest method of control consists, obviously, in interconnecting the oil valve and air valve. That arrangement is used in automatic devices for the control of temperature, but while the flow of a gas depends mainly upon its pressure and upon its specific gravity, the flow of oil depends, in addition to pressure and specific gravity, upon its viscosity, which latter varies not only with the temperature of the oil but also with its chemical composition. From these facts, it stands to reason that if a satisfactory automatic control of furnace atmosphere is to be obtained with oil as fuel, oil pressure and air pressure are not the only items which must be kept constant, but also its viscosity. Since the latter varies very much with the temperature of the oil, it is evident that automatic control of furnace atmosphere with oil fired furnaces can be obtained only if oil pressure and oil temperature are kept absolutely constant and unvarying. These statements refer to oil temperature and oil pressure at the flow controlling device and not at some other place; this distinction is important. The oil pressure may be kept constant at the pump, and yet may vary at the controlling device on account of the varying condition of the strainers which clog up as time goes on. The oil temperature may be kept constant at the heater and yet may vary at the flow-controlling device on account of varying rates of cooling of the oil, which cooling depends upon the rate at which oil flows through the pipes from the heater to the controlling device. Lack of observation of these simple facts has brought practically all atmosphere-controlling devices for oil into disrepute.

In view of these many difficulties, it is no wonder that no commercial system for control of furnace atmosphere is in use for liquid fuels. Fortunately, the eye of the heater is a better guide to furnace atmosphere, if liquid fuels are burned than it is if gaseous fuels are used. Most of the liquid fuels contain very heavy hydrocarbons,

which have a tendency to produce smoke as soon as there is a marked deficiency of air in the furnace, particularly if cold air is used for combustion. In consequence, the heater varies the air supply until the furnace atmosphere has a sufficiently hazy appearance. For a given deficiency of air, this hazy appearance varies with the temperature of the combustion air. On that account, it is very desirable that from time to time the flue gas analysis be checked by an Orsat apparatus so that the heater may be in a position to compare the appearance of the furnace atmosphere with the actual flue gas analysis. With important furnaces or for furnaces of large size it would be very desirable to provide automatic flue gas analyzing apparatus such as was before mentioned under furnace atmosphere control for gaseous fuels. The electrical instrument based upon catalytic combustion and the principle of the Wheatstone bridge seems particularly well adapted to this purpose.

For the reason above given, flue gas analyzing apparatus should be relied upon even if all of the combustion air is furnished by a blast, and if an automatic temperature control device is provided. On account of solid matter carried by the liquid fuel, it is practically impossible to maintain constant flow of oil or tar for a given opening of the restriction in the temperature controlling device. In consequence, the supply of liquid fuel varies, and the furnace atmosphere wanders away from the correct adjustment. Furnace temperature is maintained by an increased opening of the fuel and air valves, and the fuel supply is restored to its former value, while the air supply is increased. Since the change from a slightly reducing to a slightly oxidizing atmosphere is a hair-trigger adjustment, constant supervision is necessary, in spite of automatic temperature control. This statement should not be misconstrued to mean that equipment for maintaining constant oil pressure, oil temperature, and blast equipment is superfluous. On the contrary, such equipment is very necessary, because without it, the flame may change from one foot in length to six feet in length in a few minutes. After it has been adjusted back to the right length, it may become disappearingly small or even blow out. Equipment for maintaining combustion conditions constant is very necessary.

While it has apparently not been done up to the present time, it is easily imaginable that electrical flue gas analyzing equipment can be used for the automatic control of furnace atmosphere. The depressor bar instrument which now records $CO + H_2$ can be used

for varying the supply of air so that the constant flue gas analysis is maintained in the same manner in which the depressor bar recorder of a pyrometer maintains constant temperature. Such instruments would not be difficult of design, and it is hoped that someone will have the courage to develop one and put it on the market. Such a device could be used equally well for gaseous, liquid, and solid fuels. At the present time, the maintaining of constant oil pressure, constant oil temperature, constant blast pressure, and frequent cleaning of the strainers offers the greatest chances for maintaining a constant furnace atmosphere, particularly in conjunction with an automatic temperature controlling device.

The statements which were made about dampers in the discussion of the control of furnace atmosphere with gaseous fuels likewise apply to liquid fuels. By rights, there should be automatic control of the dampers, also on furnaces fired with liquid fuel. This control is intricate, for the same reasons which hold with gaseous fuels.

With solid fuels burning on a grate, control of furnace atmosphere is rather difficult, although by no means impossible. It can, at the present time, be accomplished only by correct design of the furnace and combustion chamber and by ceaseless attention of the heater. This statement applies not only to hand fired grates, but also to stoker firing. Automatic control of furnace atmosphere with coal on the grate has not yet been accomplished. It should, however, be possible to realize automatic control by means of CO_2, CO, and O_2 meters which control air admission above the fuel bed. Such devices have been proposed, but have not been introduced commercially.

With powdered coal, accurate control of furnace atmosphere is easier than with coal on the grate, because the flow of fuel can be regulated with some degree of accuracy. The difficulty consists in securing an adjustment which will proportionally vary the flow of fuel, the flow of emulsion (primary) air, and the amount of secondary air. For a constant rate of heating, these quantities can be adjusted nicely, but with variable flow, that adjustment is tedious, if made by hand. And yet, the art has not been developed sufficiently far to give us automatic control. Powdered coal presents a difficulty which does not exist with gaseous fuel, and exists only in a moderate degree with liquid fuel, namely the necessity of complete combustion in the combustion chamber. With gas, we can delay combustion and finish it in the heating chamber. With powdered coal, that

arrangement can, as a rule, not be used, because partly burned particles of coke would drop on the heating stock and mark it.

In electrically heated furnaces, the question of furnace atmosphere has not yet become acute. Such furnaces are, as a rule, used for comparatively low temperatures, that is to say, for temperatures below 1600° Fahrenheit. While scaling occurs at these temperatures, it is not excessive. For that reason, electrically heated furnaces are usually so constructed that the flow of air into, or circulation of air through the furnace is practically absent. The whole furnace is enclosed in sheet steel, and all possible precautions are taken to have a very tight-fitting door. Whatever oxygen there happens to be in the furnace at the beginning of the heating operation is soon used up, and practically no new oxygen is allowed to enter, except a little bit which leaks in by virtue of the slight vacuum which is produced by absorption of the oxygen by the steel. In any event, the total amount is limited. Observation holes are seldom necessary, particularly if automatic temperature control is used; for that reason, no oxygen enters from that source. In annealing and heat treating operations, the parts which are sent to the electric furnace have frequently been machined and still have enough of an oil skin on them to protect them from serious oxidation. Before the steel is hot enough to form scale, the oil vaporizes and burns in the furnace, absorbing the oxygen. The rest of the oil vapor breaks up into its elements, forming a reducing atmosphere which protects the steel. If the parts are not oily, a very small amount of oil sprayed over them or on the trays containing the parts would have the same effect. In this manner, a reducing atmosphere could be maintained without much trouble. An oxidizing atmosphere, if such is to be desired, could of course be maintained by allowing some air to circulate through the furnace all the time. For the maintaining of a reducing atmosphere, it would also be possible to burn a small gas flame which would soon take up the oxygen and produce a hazy atmosphere. In that case, precautions would have to be taken to prevent explosions. This problem has not yet been fully worked out, but engineers are working on it and its solution does not seem to be far off.

Discussion

Dr. Blaisdell [Before reading paper]: I would like to make a comment, the title of the paper is "Control of Furnace Atmosphere."

It is to be regretted that Professor Trinks is not able to be here to read the paper himself. It means so much more if the man who wrote the paper himself can read it because he can lay emphasis where emphasis is to be laid and he can answer questions. I know nothing about furnace atmosphere other than what is in this paper, but Professor Trinks will be glad to take it up with you, any one who so desires, either by telephone or by letter.

INSULATION OF SUPERHEATED STEAM SURFACES

By R. H. HEILMAN *

Read at the Pittsburgh Meeting, December 6, 1924

The continued use of superheated steam in chemical processes, oil stills, power plants, etc., and the present tendency to increase the temperature higher and higher, make it imperative that all users of superheated steam study carefully the necessity of insulating all exposed surfaces in accordance with a scientific standard of thickness for pressure.

This paper presents tables and curves which show the enormous savings that can be effected by insulating high-temperature surfaces; it also includes the type and thickness of insulation that should be used under various high-temperature conditions.

Heat Losses from Bare Surfaces

In order to estimate the saving that can be effected by insulating an exposed surface, it is first necessary to know the amount of heat lost from the bare surface.

A large portion of the exposed surfaces used in the chemical industries is in pipes, boilers, stills and drums.

Considerable work has been done by various investigators on the determination of heat losses from bare steel pipes. For the most part however the researches were carried out at low temperatures or for one pipe size only.

In view of this fact, Mellon Institute has carried on the work to higher temperatures and on three pipe sizes, namely, 1-, 3- and 10-inch standard steel pipes, so as to be able to derive empirical formulas which can be applied to the various pipe sizes used in the industries.

The electrical method of testing is used at the Institute, because it has proved to be the most accurate and very easily controlled. The apparatus now used is the gradual development of seven years work on heat insulations, and the precision of the present method has been checked in several ways and found to be entirely satis-

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factory. The apparatus [1, 2] used has been described in other papers so that a description is unnecessary here.

When conducting tests on bare pipes it is very desirable that the room temperature remain constant throughout the work, for the rate of heat loss is dependent upon the absolute temperature as well as upon the temperature difference. The 1-inch pipe was

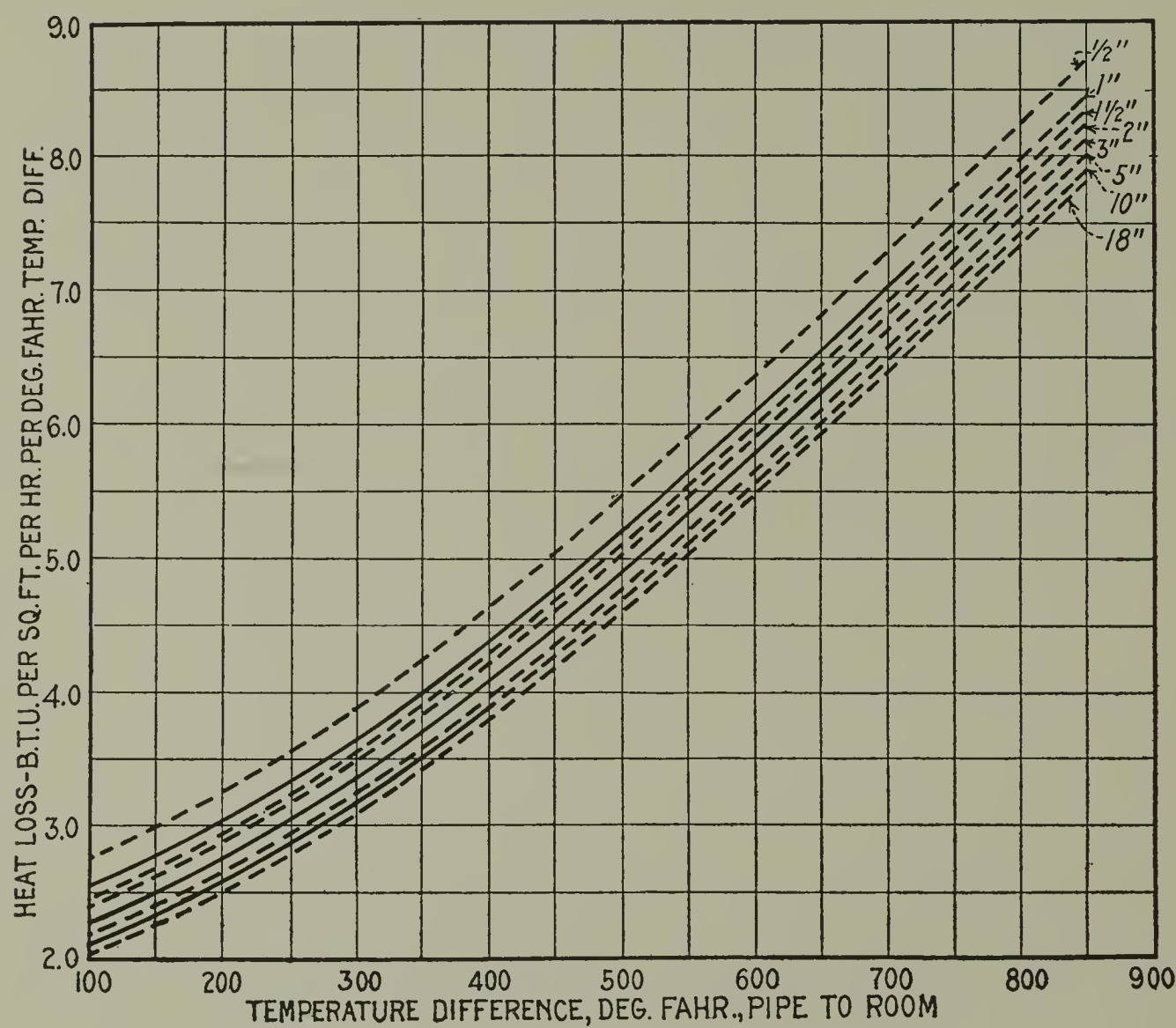

Fig. 1

selected for test at the higher temperature, as the relatively small amount of heat loss from a 1-inch pipe could not greatly affect the room temperature. This pipe was run up to a temperature of 800° F. The average room temperature throughout this test was 81° F., and the temperature did not vary more than 1.8° F. during its progress. The 3-inch pipe was run up to a temperature of 760° F., and the 10-inch pipe to a temperature of 472° F.

The values for the higher temperatures on the 10-inch pipe

[1] *Trans. A. S. M. E.*, vol. 44 (1922), p. 300.

[2] *Mech. Eng.*, vol. 46, No. 10, October (1924), p. 593.

were obtained by extending the curve parallel to the curves obtained for the 1-inch and the 3-inch pipes. This procedure was necessary because of the fact that the larger pipe could not be raised to the higher temperatures without considerably increasing the temperature of the room.

The experimental curves for the 1-, 3-, and 10-inch pipes are shown in the solid lines in Fig. 1. The dotted lines for the other pipe sizes shown were obtained by interpolation and extrapolation. The total heat loss from bare steel pipes as obtained in this investigation can be expressed approximately by the empirical equation

$$H = 3320 \frac{77 + Td - 103D^{0.11}}{103D^{0.11} - Td + 1020} \tag{1}$$

or

$$Td = \frac{H - 250}{0.00098H + 3.25} + 103D^{0.11}, \tag{2}$$

in which H = B.T.U. loss per hour per square foot of pipe surface,

D = outer diameter of pipe, in inches,

Td = temperature difference between pipe surface and room, °F.

This equation is approximately accurate for pipe sizes from $\frac{1}{2}$-inch to 30-inch.

The accurate determination of the heat losses from flat surfaces presents a very difficult problem, because the heat loss per unit area varies greatly with the size and position of the body. The loss from the surface in a horizontal position is entirely different for the same surface in a vertical position. Also, the loss is different for the same flat surface facing downwards than for it facing upwards. This is due entirely to the modification of the convection currents caused by the different positions of the flat surface.

Tests made by the National Physical Laboratory [3] on plane surfaces show that the rate of loss in the vertical position is practically a mean of the rates of the two positions of the horizontal surface facing upwards and downwards. The rate of heat loss is naturally least in the horizontal position facing downwards.

The results of the investigation conducted by the National Physical Laboratory also seem to indicate that for large pipes above

[3] Griffiths and Davis, "The Transmission of Heat by Radiation and Conviction," Special Report *9*, Department of Scientific and Industrial Research, London, England.

12-inches in diameter in a horizontal position the heat loss per unit area is roughly independent of size and curvative, appearing the same for cylinders and vertical plates whose heights are greater than 12 inches.

It would therefore seem that the approximate loss from flat surfaces could be taken as equal to that of a large diameter cylinder. In most cases the area of vertical surfaces and horizontal surfaces facing upwards will greatly exceed the area of horizontal surfaces facing downwards, so that this factor should be taken into account when making calculations. Most of the work that has been done on plane surfaces has been at comparatively low temperatures; and while the results obtained could possibly be extended to higher temperatures with little error, it is hoped that future investigations will be carried out at both low and high temperatures.

Thermal Conductivity of Insulating Materials

The true meaning of the term "thermal conductivity" of a material is the number of heat units transferred by conduction per unit area, across unit thickness, per degree difference of temperature between the faces, the direction of heat flow being perpendicular to these faces. In terms of the units generally used in power plant practice, this is equivalent to the heat transmitted in B.T.U. per hour through 1 square foot of material 1 inch thick and having 1° F. temperature difference between its faces.

The thermal conductivities of the various types of heat insulation now on the market have been determined and are included in this report. The thermal conductivity has been calculated from the heat losses through the insulations by means of the formula

$$K = h \frac{r_2 \log_e \frac{r_2}{r_1}}{T_1 - T_2} \tag{3}$$

in which h = heat loss in B.T.U. per sq. ft. of outer surface of insulation.

r_1 = radius of inner surface of covering in inches.
r_2 = radius of outer surface of covering in inches.
T_1 = temperature °F. at inner surface of covering.
T_2 = temperature °F. at outer surface of covering.

The method used in testing has been described in former papers [4]

[4] *Mech. Eng.*, vol. 46, No. 10, October (1924), p. 593.

and will therefore not be given here. The value of T_2 was measured with thermocouples and checked against the equation

$$Td = \frac{272.5h}{h + \frac{564}{D^{0.19}}}, \tag{4}$$

which was derived by the author from former experiments. It was found that this equation checked almost exactly with the results obtained during the investigation. The above equation expresses the heat loss in B.T.U. per sq. ft. from unpainted horizontal canvas cylinders in terms of the temperature difference °F. between the canvas surface and the room temperature and in terms of the outside diameter of the cylinder in inches. The use of this canvas surface equation materially reduces the labor involved in making the thermal conductivity calculations.

TABLE I

VALUES OF $\frac{564}{D^{.19}}$

D	$\frac{564}{D^{.19}}$	D	$\frac{564}{D^{.19}}$	D	$\frac{564}{D^{.19}}$	D	$\frac{564}{D^{.19}}$	D	$\frac{564}{D^{.19}}$
3″	458	5.0″	415	8.5″	375	12.0″	351	18.0″	325
3.25″	451	5.5″	408	9.0″	371	12.5″	349	19.0″	322
3.50″	445	6.0″	401	9.5″	367	13.0″	346	20.0″	319
3.75″	439	6.5″	395	10.0″	364	14.0″	341	21.0″	316
4.00″	433	7.0″	390	10.5″	361	15.0″	337	22.0″	313
4.25″	428	7.5″	385	11.0″	357	16.0″	333	23.0″	310
4.50″	423	8.0″	380	11.5″	354	17.0″	329	24.0″	308

It has been found during this investigation that the over-all heat loss curves of all the various types of insulations tested followed practically a straight line law. By combining the over-all loss curves with the surface loss curves, it was found that the resulting thermal conductivity curves deviated from a straight line law by less than one per cent.

It can be proved mathematically when the conductivity of a material is a linear function of the temperature that the equivalent conductivity for the whole thickness of the insulation is equal to the conductivity corresponding to the arithmetic mean of the two surface temperatures.

Accordingly the conductivity values obtained for the various

materials have been plotted against the mean of the two surface temperatures, as shown in Figs. 2 and 3.

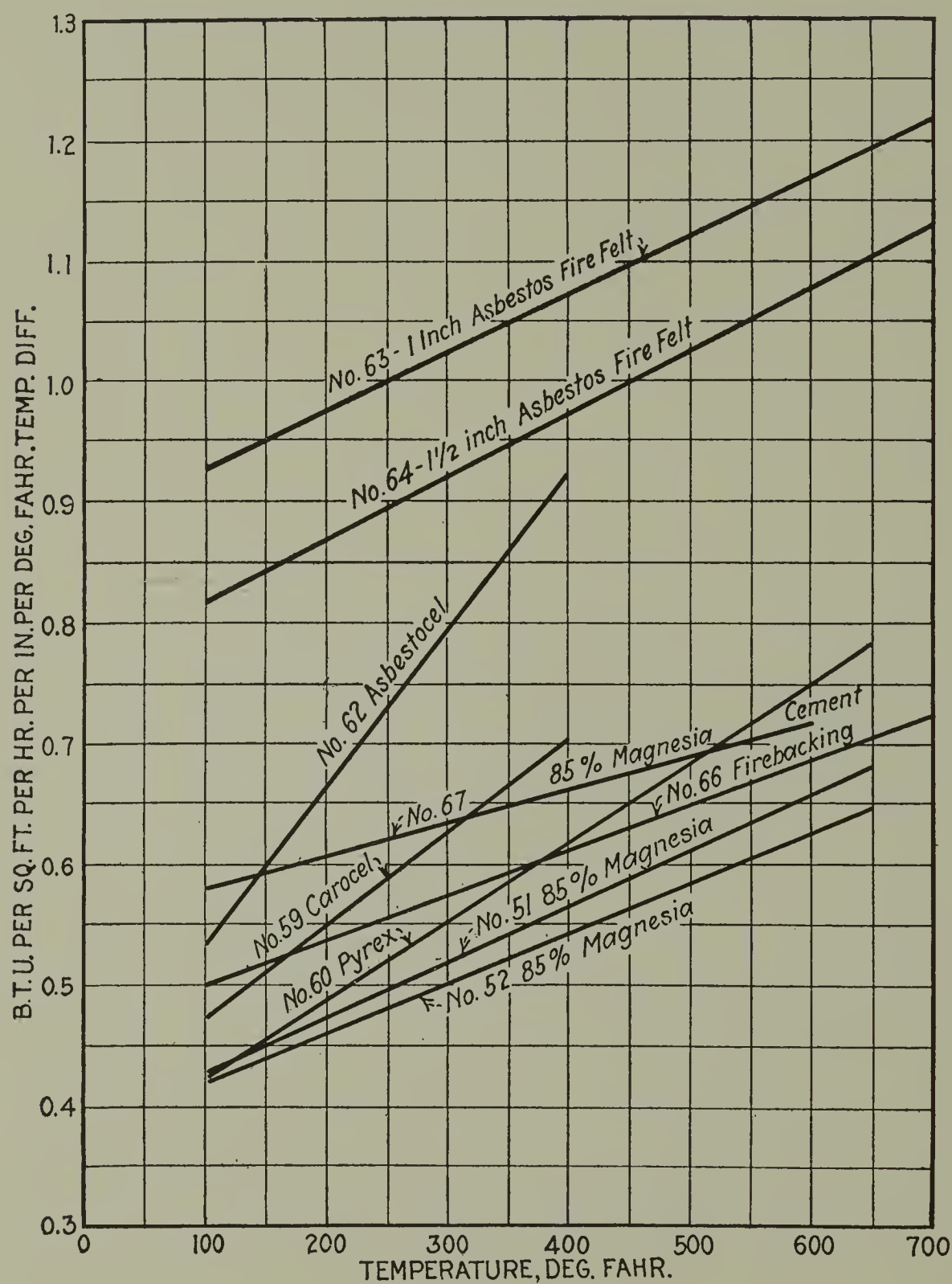

FIG. 2

This method of plotting the findings gives results that are sufficiently accurate for all engineering purposes or in fact for the most exacting comparisons, because the error involved in this assumption is less than one per cent.

The curves shown in Figs. 2 and 3 were obtained from one hundred conductivity tests on commercial insulations 1, 2, and 3 inches thick.

Where more than one thickness of a given brand of material was tested, the conductivity for the average of all the coverings of a given thickness tested was calculated for each thickness, and the

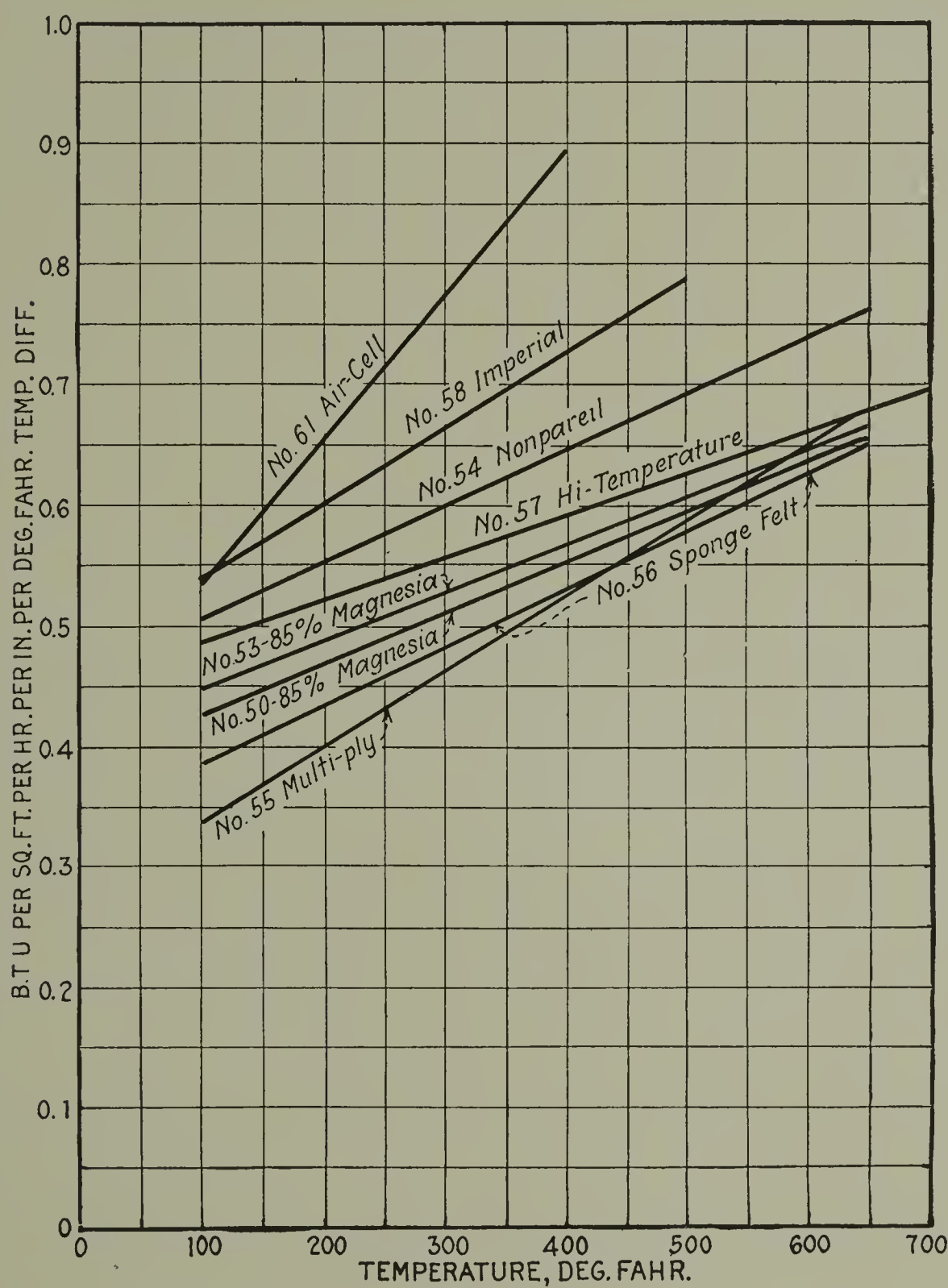

FIG. 3

average of the conductivity curves for all the thicknesses tested was taken as the true conductivity of the material. For instance, in the case of Nonpareil covering, where 1-, 2-, and 3-inch thicknesses were tested, conductivity curves were calculated for 1-, 2-, and 3-inch thicknesses, and the average of these three curves was

taken as the true conductivity curve for this product. This method was followed for all of the coverings tested, with the exception of "Asbestos Fire-Felt," in which case two separate conductivity curves are given, one for material 1-inch thick and the other for material 1.5-inches thick. The construction of "Asbestos Fire-Felt" is such that a greater proportion of hard, and consequently better conducting, material is contained in the covering 1-inch thick. This condition results in the thermal conductivity curve for the material 1-inch thick being higher than the curve for the material 1.5-inches thick.

The thermal conductivity curves for the following materials are included in Figs. 2 and 3.

No. 50—85% Magnesia No. 1. Average of 6 tests.
No. 51—85% Magnesia No. 2. Average of 6 tests.
No. 52—85% Magnesia No. 3. Average of 7 tests.
No. 53—85% Magnesia No. 4. Average of 6 tests.
No. 54—Nonpareil. Average of 6 tests.
No. 55—Carey Multi-Ply. Average of 8 tests.
No. 56—Johns-Manville Asbestos-Sponge Felted. Average of 11 tests.
No. 57—Carey Hi-Temp. Average of 7 tests.
No. 58—Watson Imperial. Average of 2 tests.
No. 59—Carey Carocel. Average of 6 tests.
No. 60—Carey Pyrex. Average of 6 tests.
No. 61—Carey Air Cell. Average of 9 tests.
No. 62—Johns-Manville Asbestocel. Average of 4 tests.
No. 63—Johns-Manville Asbestos Fire-Felt, 1-inch thick. Average of 2 tests.
No. 64—Johns-Manville Asbestos Fire-Felt, 1.5-inches thick. Average of 2 tests.
No. 65—National Magnesia Mfg. Co. Firebacking covering. Average of 7 tests.
No. 66—85% Magnesia cement. Average of 5 tests.

Insulations for Superheated Steam Temperatures

The present tendency to increase the pressure and temperature of steam in power plants, industrial plants, oil refineries, chemical processes, etc., has caused the manufacturers of heat insulation to increase the heat-resisting properties of their products, so that they will be suitable for the increased temperatures to which they are

subjected. Several years ago the well known 85 per cent magnesia covering was almost the standard for all types of installations. To-day, however, the steam temperatures have increased to such an extent that 85 per cent magnesia when used to insulate these high temperature lines has to be first protected by some other type of covering which has higher heat-resisting properties and which is capable of reducing the temperature at the inner surface of the magnesia to a point where the physical structure of the magnesia will not be destroyed.

There are several types of covering now on the market which can be used as an inner layer on superheated steam lines. Four well known types for temperatures as high as 900 to 1,000° F. are Carey "Hi-Temp," Armstrong "Nonpareil," National Magnesia "Firebacking," and J.-M. "Fire-Felt" or Carey "Felted-Fibre."

From an inspection of Figs. 2 and 3 it will be found that the thermal conductivity of "Fire-Felt" is considerably higher than that of "Hi-Temp," "Nonpareil" or "Firebacking." Unless it could be purchased at considerably less than either of the other three it would not be economical to use it. In general therefore it can be considered that either of the three above mentioned coverings will be used as the first layer or as the entire thickness of the installation. It is usual practice to use either 85 per cent magnesia, "Multi-Ply" or "Asbesto-Sponge Felt" over the first high temperature layer. While the insulating value of any or all of these combinations can be obtained from Figs. 2 and 3, the question is constantly arising as to whether the various types of insulations are suitable for the temperatures for which they are recommended. This question is a rather difficult one to answer. It is very hard to say, for example, what the crushing strength of a particular type of covering should be to render it unsatisfactory as an insulation for a specified temperature. However, a great many tests on various types of insulations have shown that, unless the material is considerably damaged by the heat so that it has a tendency to disintegrate and powder, the thermal efficiency will not be impaired. To illustrate, it is well known that 85 per cent magnesia starts to calcine at about 550° F., but a great many tests have shown that the calcination actually increases the efficiency of the covering up to a point where the covering becomes so weak that it disintegrates and breaks up. After this point is reached, the efficiency becomes impaired not by any chemical effect on the calcined magnesia but on

account of the physical disintegration that has occurred. The real test then to determine the fitness of a given type of insulation for a certain specified temperature is not a chemical analysis or a loss in weight test but some physical test that will determine the strength and shrinkage of the material when exposed to that particular temperature.

TABLE II

EFFECT OF HEATING

Material	Total Crushing Strength. Lbs. 2″ x 2″ x 1½″			Transverse Strength. Lbs. 14″ x 6″ x 1½″. 10″ Span			Modulus of Rupture. Lbs. Per Sq. In.			Lineal Shrinkage Per Cent	
	Before Heating	500° F.	800° F.	Before Heating	500° F.	800° F.	Before Heating	500° F.	800° F.	500° F.	800° F.
85% magnesia..	600	538		70	68		70	68		0.5	
Hi-Temp.....	1000+		700	140		70	140		70		3.0
Nonpareil.....	1000+		1000+	110		60	110		60		0.3
Firebacking....	550		295	80		50	80		50		0.6

TABLE II*A*

THERMAL CONDUCTIVITY

Material	Mean Temperature, Deg. Fahr. Between Inner and Outer Surfaces				
	500	550	600	650	700
Hi-Temp.....	0.625	0.642	0.660	0.678	0.695
Nonpareil.....	0.690	0.714	0.738	0.760	0.783
Firebacking.....	0.650	0.669	0.687	0.705	0.724

Since 85 per cent magnesia has been the standard covering of the United States Navy since 1887 and has been found in this lengthy service to have sufficient strength for handling, etc., the author is of the opinion that any other type of covering to be used under high temperature conditions should at least have, after being subjected to the temperature for which it is intended, the strength which 85 per cent magnesia has after it has been exposed to a temperature of, say, 500° F.

Table II shows the results of the average of 10 tests on various types of insulation when new and when subjected to various temperatures in an electric oven. It should be understood that an oven test is a much more severe test than would occur under actual

operating conditions at the same temperature. The sample in the oven test is thoroughly heated through at the temperature of the oven, while under practical conditions only a very small thickness of the inner surface of the covering is heated to the maximum temperature.

The crushing strength was determined by placing the samples 2 in. x 2 in. x 1.5 in. thick in a small hydraulic press and applying pressure to the ram until the material showed the first signs of cracking. The gage pressure was taken at this point and was considered as the crushing strength of the sample. The limit of the gage was 1,000 lbs.

The transverse strength was determined by placing the samples 6 in. x 14 in. x 1.5 in. thick in the press on 10-inch centers and applying pressure to the ram until the material broke in two.

The modulus of rupture for the various samples was computed from the formula

$$f = \frac{WL}{4} \cdot \frac{1}{Z} \cdot \tag{6}$$

In which

W = the central load in pounds.
L = the length of span in inches.
Z = the modulus of the section.
f = the modulus of rupture in pounds per square inch.

From an inspection of Table II it will be seen that the "Firebacking" covering fell below the 85 per cent magnesia covering in strength, while the "Hi-Temp" covering, after being subjected to an oven heat of 800° F., had a greater shrinkage than the 85 per cent magnesia covering. As mentioned before, however, the oven test is very severe and from practical considerations the author is of the opinion that either covering is suitable for temperatures up to 800° F. and probably to 1,000° F.

When testing the conductivity of "Firebacking," it was found to have sufficient strength for handling when the inner surface only was subjected to the high temperature. Also an installation of "Hi-Temp" which had been on an oil line at 900° F. for a period of 8 months showed a shrinkage of only 3/16 inch in a 36-inch section or about 0.5 of 1 per cent.

It can therefore be concluded that as far as strength and shrinkage after heating are concerned either of the three high temperature

insulations tested can be used as an inner layer for superheated steam temperatures. Table II*A* shows the conductivity of the three high temperature insulations at mean temperatures of 500° to 700° F.

Savings Resulting from Proper Insulation of Superheated Steam Surfaces

The main object of this paper is to show the relatively short time required to repay the original cost of the installations and the relatively large return per year on the investment which can be effected by the proper insulation of superheated steam surfaces. The fact that a 4-inch thickness of pipe covering, when applied to an 18-inch pipe operating at a temperature of 900° F., will pay for itself in a period of 21 days with steam at only 35 cents per 1,000,000 B.T.U., is of sufficient importance to arouse the interest of any engineer who is at all concerned with the conservation of fuel.

There are many instances where the proper insulation of exposed or under-insulated surfaces would repay the original cost many times over in one year; for example, exposed fittings, under-insulated steam lines, boilers, ovens, and temporary heating appliances used in chemical and plant laboratories. The fact that pipes are covered does not end the possibility of heat losses. It is the poorest economy to use a minimum thickness of covering on high pressure lines and apparatus when the use of a thicker covering will not only result in greater efficiency, but will quickly pay for itself in the extra heat saved. The length of time required to repay the original cost of the investment depends of course on the cost of the heat which would otherwise be lost and upon the cost of the covering as applied together with the annual fixed charges.

The cost of heat varies considerably in various plants and localities, so that calculations based on one cost of steam would obviously be applicable only to that particular case. Some of the factors which influence the cost of steam are cost of fuel, heat content of the fuel, efficiency of the installation, method of firing, load factor, charges against the investment in boiler plant, and operating charges.

Some of the factors which influence the cost of the insulation as applied are initial cost of material, labor rate per hour, amount of cement work compared with straight pipe and blocks, number of fittings and bends compared with straight pipe, accessibility of

TABLE III

Time Required to Repay Original Cost and Savings Per Year

Pipe Temperature °F.		500					550					600				
	Fuel Cost	.15	.20	.25	.30	.35	.15	.20	.25	.30	.35	.15	.20	.25	.30	.35
2 in. Pipe	Material	2 in. th. Mg.					2 in. th. Mg.					1 in. th. H-T., $1\frac{1}{2}$ in. th. Mg.				
Covering and application list	*Months Required*	8.50	6.39	5.10	4.24	3.63	6.9	5.2	4.2	3.5	2.9	7.7	5.7	4.6	3.8	3.3
	Saving per yr.	1.28	1.75	2.22	2.70	3.17	1.60	2.18	2.76	3.14	3.92	1.93	2.63	3.34	4.03	4.74
Covering and application list − 20%	*Months Required*	6.80	5.10	4.08	3.47	2.90	5.6	4.2	3.3	2.8	2.4	6.1	4.6	3.7	3.1	2.9
	Saving per yr.	1.31	1.78	2.25	2.73	3.20	1.63	2.21	2.79	3.37	3.95	1.99	2.69	3.40	4.09	4.80
4 in. Pipe	Material	D. S. Mg.					D. S. Mg.					1 in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	6.5	4.8	3.9	3.2	2.8	5.3	4.0	3.2	2.6	2.3	7.1	5.3	4.2	3.7	3.1
	Saving per yr.	2.42	3.29	4.15	5.02	5.89	3.01	4.07	5.14	6.20	7.27	3.21	4.91	6.31	7.51	8.81
Covering and application list − 20%	*Months Required*	5.2	3.9	3.1	2.6	2.2	4.2	3.2	2.5	2.1	1.8	5.7	4.2	3.4	2.8	2.4
	Saving per yr.	2.47	3.34	4.20	5.07	5.94	3.06	4.12	5.19	6.25	7.32	3.67	4.97	6.37	7.57	8.87
6 in. Pipe	Material	3 in. th. Mg.					3 in. th. Mg.					1 in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	8.5	6.3	5.1	4.2	3.5	6.9	5.2	4.1	3.4	2.9	5.9	4.4	3.5	2.9	2.5
	Saving per yr.	3.48	4.76	6.05	7.32	8.60	4.35	5.93	7.50	9.07	10.65	5.34	7.24	9.14	11.04	12.94
Covering and application list − 20%	*Months Required*	6.6	5.1	4.0	3.4	2.9	5.5	4.1	3.3	2.7	2.4	4.7	3.5	2.8	2.4	2.0
	Saving per yr.	3.55	4.83	6.12	7.39	8.69	4.42	6.00	7.57	9.14	10.72	5.41	7.31	9.21	11.11	12.01
8 in. Pipe	Material	3 in. th. Mg.					3 in. th. Mg.					$1\frac{1}{2}$ in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	7.6	5.7	4.6	3.8	3.3	6.2	4.6	3.7	2.1	2.7	6.3	4.7	3.8	3.1	2.7
	Saving per yr.	4.55	6.21	7.86	9.52	11.17	5.70	7.74	9.77	11.80	13.84	6.94	9.42	11.90	14.37	16.86
Covering and application list − 20%	*Months Required*	6.1	4.6	3.7	3.8	2.6	5.0	3.7	3.0	2.5	2.1	5.0	3.8	3.0	2.5	2.2
	Saving per yr.	4.63	6.29	7.94	9.60	11.25	5.78	7.82	9.85	11.88	13.92	7.03	9.51	11.99	14.46	16.95
10 in. Pipe	Material	3 in. th. Mg.					3 in. th. Mg.					$1\frac{1}{2}$ in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	7.1	5.4	4.2	3.5	3.0	5.8	4.3	3.5	2.9	2.5	6.0	4.6	3.6	3.0	2.6
	Saving per yr.	5.73	7.79	9.85	11.93	13.99	7.13	9.65	12.19	14.73	17.26	8.65	11.72	14.81	17.90	21.00

TABLE III—*Continued*

Pipe Temperature ° F.		500					550					600				
	Fuel Cost	.15	.20	.25	.30	.35	.15	.20	.25	.30	.35	.15	.20	.25	.30	.35
10 in. Pipe	Material	3 in. th. Mg.					3 in. th. Mg.					$1\frac{1}{2}$ in. th. H-T., 2 in. th. Mg.				
Covering and application list — 20%	*Months Required*	5.6	4.2	3.4	2.8	2.4	4.6	3.5	2.8	2.3	2.0	4.8	3.6	2.9	2.4	2.1
	Saving per yr.	5.82	7.88	9.94	12.02	14.08	7.22	9.74	12.28	14.82	17.35	8.77	11.84	14.93	18.02	21.12
12 in. Pipe	Material	$3\frac{1}{2}$ in. th. Mg.					$3\frac{1}{2}$ in. th. Mg.					$1\frac{1}{2}$ in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	7.8	5.9	4.7	3.9	3.4	6.4	4.7	3.8	3.2	2.7	5.5	4.1	3.3	2.7	2.4
	Saving per yr.	6.71	9.15	11.59	14.06	15.49	8.42	11.42	14.43	17.46	20.47	10.28	13.93	17.56	21.25	24.85
Covering and application list — 20%	*Months Required*	6.3	4.7	3.8	3.1	2.7	5.1	3.8	3.1	2.5	2.2	4.4	3.3	2.5	2.2	1.9
	Saving per yr.	6.84	9.28	11.72	14.19	15.62	8.55	11.55	14.56	17.59	20.60	10.41	14.06	17.69	21.38	24.93
14 in. Pipe	Material	$3\frac{1}{2}$ in. th. Mg.					$3\frac{1}{2}$ in. th. Mg.					$1\frac{1}{2}$ in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	8.2	6.1	4.9	4.1	3.5	6.6	5.0	4.0	3.8	2.8	5.4	4.1	3.2	2.7	2.3
	Saving per yr.	7.29	9.97	12.64	15.29	17.99	9.14	12.41	15.69	18.99	22.29	11.58	15.68	19.78	23.88	27.98
Covering and application list — 20%	*Months Required*	6.5	4.9	3.9	3.3	2.8	5.3	4.0	3.2	2.7	2.3	4.3	3.2	2.6	2.2	1.9
	Saving per yr.	7.43	10.11	12.78	15.43	18.13	9.28	12.55	15.83	19.13	22.43	11.72	15.82	19.92	24.02	27.12
16 in. Pipe	Material	$3\frac{1}{2}$ in. th. Mg.					$3\frac{1}{2}$ in. th. Mg.					$1\frac{1}{2}$ in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	8.8	6.6	5.3	4.4	3.8	6.5	4.9	3.9	3.3	2.8	5.4	4.1	3.3	2.7	2.3
	Saving per yr.	7.52	10.30	13.10	15.85	19.60	10.40	14.15	17.90	21.60	25.35	12.75	17.28	21.80	26.30	30.84
Covering and application list — 20%	*Months Required*	7.0	5.3	4.2	3.5	3.0	5.2	3.9	3.1	2.6	2.2	4.4	3.3	2.6	2.2	1.9
	Saving per yr.	7.69	10.47	13.27	16.02	19.77	10.57	14.32	18.07	21.77	25.52	12.92	17.44	21.96	26.46	31.00
18 in. Pipe	Material	$3\frac{1}{2}$ in. th. Mg.					$3\frac{1}{2}$ in. th. Mg.					$1\frac{1}{2}$ in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	7.8	5.8	4.7	3.9	3.3	6.3	4.7	3.8	3.2	2.7	5.3	4.0	3.2	2.6	2.3
	Saving per yr.	9.34	12.76	16.16	19.56	22.96	11.72	15.90	20.10	24.30	28.50	14.39	19.49	24.57	29.65	34.73
Covering and application list — 20%	*Months Required*	6.2	4.7	3.7	3.1	2.7	5.0	3.8	3.0	2.5	2.2	4.2	3.2	2.5	2.1	1.8
	Saving per yr.	9.51	12.93	16.32	19.72	23.12	11.89	16.07	20.27	24.47	28.57	14.56	19.66	24.74	29.82	34.90
Flat Surface	Material	4 in. th. Mg.					4 in. th. Mg.					$1\frac{1}{2}$ in. th. H-T., $2\frac{1}{2}$ in. th. Mg.				
Covering and application list	*Months Required*	7.0	5.2	4.2	3.5	3.0	5.7	4.2	3.4	2.8	2.4	4.7	3.5	2.8	2.3	2.0
	Saving per yr.	1.91	2.60	3.28	3.98	4.66	2.38	3.23	4.08	4.94	5.78	2.92	3.95	4.98	6.00	7.03
Covering and application list — 20%	*Months Required*	5.6	4.2	3.3	2.8	2.4	4.5	3.4	2.7	2.3	1.9	3.7	2.8	2.2	1.9	1.6
	Saving per yr.	1.95	2.64	3.33	4.02	4.70	2.42	3.27	4.12	4.98	5.82	2.96	3.99	5.02	6.04	6.07

TABLE IV

Time Required to Repay Original Cost and Savings Per Year

Pipe Temperature ° F.		650					700					750				
	Fuel Cost	.15	.20	.25	.30	.35	.15	.20	.25	.30	.35	.15	.20	.25	.30	.35
2 in. Pipe	Material	1 in. th. H-T., 1½ in. th. Mg.					1 in. th. H-T., 1½ in. th. Mg.					1 in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	6.3	4.7	3.8	3.2	2.7	5.5	4.1	3.3	2.7	2.3	5.9	4.5	3.6	3.0	2.5
	Saving per yr.	2.38	3.24	4.09	4.94	5.79	2.77	3.75	4.73	5.71	6.69	3.25	4.40	5.56	6.72	7.88
Covering and application list − 20%	*Months Required*	5.0	3.8	3.0	2.5	2.2	4.4	3.3	2.6	2.2	1.9	4.7	3.6	3.8	2.4	2.0
	Saving per yr.	2.44	3.30	4.15	5.00	5.85	2.83	3.81	4.79	5.77	6.75	3.29	4.44	5.60	6.76	7.92
4 in. Pipe	Material	1 in. th. H-T., 2 in. th. Mg.					1 in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	5.9	4.5	3.6	3.0	2.5	5.0	3.8	3.1	2.5	2.2	5.1	3.8	3.0	2.5	2.2
	Saving per yr.	4.36	5.90	7.49	9.03	10.60	5.20	7.04	8.86	10.70	12.54	6.13	8.29	10.45	12.60	14.75
Covering and application list − 20%	*Months Required*	4.7	3.6	2.8	2.4	2.0	4.0	3.0	2.4	2.0	1.7	4.0	3.0	2.4	2.0	1.7
	Saving per yr.	4.42	5.46	7.55	9.09	10.66	5.26	7.10	8.92	10.76	12.60	6.20	8.36	10.51	12.67	14.82
6 in. Pipe	Material	1 in. th. H-T., 2 in. th. Mg.					1 in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	4.9	3.7	2.9	2.5	2.1	4.2	3.1	2.5	2.1	1.8	4.2	3.1	2.5	2.1	1.8
	Saving per yr.	6.46	8.73	10.99	13.26	15.54	7.68	10.34	13.06	15.71	18.39	8.99	12.15	15.28	18.42	21.57
Covering and application list − 20%	*Months Required*	3.9	2.9	2.4	2.0	1.7	3.3	2.5	2.0	1.7	1.4	3.8	2.5	2.0	1.7	1.4
	Saving per yr.	6.53	8.80	11.06	13.33	15.61	7.75	10.41	13.13	15.78	18.46	9.09	12.25	15.38	18.52	21.67
8 in. Pipe	Material	1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	5.3	4.0	3.2	2.6	2.3	4.5	3.3	2.7	2.2	1.9	3.4	2.6	2.0	1.7	1.5
	Saving per yr.	8.38	11.34	14.30	17.26	20.72	10.00	13.50	17.00	19.50	24.00	11.74	17.84	19.92	24.21	28.09
Covering and application list − 20%	*Months Required*	4.2	3.2	2.5	2.1	1.8	3.6	2.7	2.1	1.8	1.5	3.0	2.3	1.8	1.5	1.3
	Saving per yr.	8.47	11.43	14.39	17.35	20.81	10.09	13.59	17.09	19.59	24.09	11.84	17.94	20.02	24.31	28.19
10 in. Pipe	Material	1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	5.1	3.8	3.0	2.5	2.2	4.3	3.2	2.6	2.1	1.8	3.7	2.8	2.2	1.8	1.6
	Saving per yr.	10.44	14.10	17.80	21.50	25.10	12.43	17.78	21.10	25.50	29.88	14.63	19.70	24.80	29.85	34.90

TABLE IV—*Continued*

Pipe Temperature ° F.		650					700					750				
	Fuel Cost	.15	.20	.25	.30	.35	.15	.20	.25	.30	.35	.15	.20	.25	.30	.35
10 in. Pipe	Material	1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.				
Covering and application list—20%	*Months Required*	4.0	3.0	2.5	2.0	1.7	3.4	2.6	2.1	1.7	1.5	2.9	2.2	1.8	1.5	1.3
	Saving per yr.	10.55	14.21	17.91	21.61	25.21	12.55	17.90	21.22	25.62	29.92	14.75	19.82	24.92	29.92	35.02
12 in. Pipe	Material	1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.					2 in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	4.8	3.6	2.9	2.3	1.9	3.9	2.9	2.3	1.9	1.7	4.1	3.1	2.4	2.0	1.8
	Saving per yr.	11.90	16.10	20.30	24.45	28.65	14.80	19.95	25.10	30.25	35.40	17.30	23.30	29.30	35.35	41.40
Covering and application list—20%	*Months Required*	3.9	2.9	2.2	1.9	1.6	3.1	2.3	1.9	1.6	1.3	3.3	2.4	2.0	1.6	1.4
	Saving per yr.	12.03	16.23	20.43	24.58	28.78	14.93	20.08	25.23	30.38	35.53	17.46	23.46	29.46	35.51	41.56
14 in. Pipe	Material	1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.					2 in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	4.6	3.5	2.8	2.3	2.0	3.9	3.0	2.4	2.0	1.7	4.2	3.0	2.4	2.0	1.7
	Saving per yr.	13.68	18.33	23.08	27.88	32.58	16.18	21.78	27.38	33.08	38.18	18.94	25.49	32.09	38.83	45.24
Covering and application list—20%	*Months Required*	3.7	2.8	2.2	1.9	1.6	3.1	2.4	1.9	1.6	1.3	3.2	2.4	1.9	1.6	1.4
	Saving per yr.	13.82	18.47	23.22	28.02	32.72	16.32	21.92	27.52	33.22	38.82	19.11	25.66	32.26	39.01	45.41
16 in. Pipe	Material	1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.					2 in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	4.6	3.4	2.7	2.3	2.0	3.8	2.9	2.3	1.9	1.6	3.9	2.9	2.3	1.9	1.7
	Saving per yr.	15.40	20.80	26.20	31.60	37.00	18.40	24.80	31.20	37.60	44.00	21.55	29.15	36.65	44.15	51.65
Covering and application list—20%	*Months Required*	3.6	2.7	2.2	1.8	1.6	3.0	2.3	1.8	1.5	1.3	3.1	2.3	1.9	1.6	1.3
	Saving per yr.	15.56	20.96	26.36	31.76	37.16	18.56	24.96	31.36	37.76	44.16	21.74	29.34	36.84	44.34	51.84
18 in. Pipe	Material	1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.					2 in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	4.4	3.3	2.6	2.2	1.9	3.7	2.8	2.2	1.9	1.6	3.7	2.8	2.2	1.9	1.6
	Saving per yr.	17.35	23.43	29.53	35.63	41.63	20.73	27.93	35.13	41.38	49.63	24.28	32.73	41.18	49.58	58.48
Covering and application list—20%	*Months Required*	3.5	2.6	2.1	1.8	1.5	3.0	2.2	1.8	1.5	1.3	3.0	2.2	1.8	1.5	1.3
	Saving per yr.	17.52	23.60	29.70	35.80	41.80	20.90	28.10	35.30	41.55	49.80	24.48	32.93	41.38	49.78	59.18
Flat Surface	Material	1½ in. th. H-T., 2½ in. th. Mg.					1½ in. th. H-T., 2½ in. th. Mg.					2 in. th. H-T., 2½ in. th. Mg.				
Covering and application list	*Months Required*	3.9	2.9	2.3	2.0	1.8	3.3	2.5	2.0	1.7	1.4	3.2	2.4	1.9	1.6	1.4
	Saving per yr.	3.52	4.74	5.98	7.20	7.94	4.19	5.64	7.09	8.54	9.99	4.93	6.64	8.35	10.05	11.77
Covering and application list—20%	*Months Required*	3.1	2.4	1.9	1.6	1.4	2.7	2.0	1.6	1.3	1.1	2.5	1.9	1.5	1.2	1.1
	Saving per yr.	3.56	4.78	6.02	7.24	7.98	4.23	5.68	7.13	8.58	10.03	4.97	6.68	8.39	10.09	11.81

TABLE V

TIME REQUIRED TO REPAY ORIGINAL COST AND SAVINGS PER YEAR

Pipe Temperature °F.		800					850					900				
	Fuel Cost	.15	.20	.25	.30	.35	.15	.20	.25	.30	.35	.15	.20	.25	.30	.35
2 in. Pipe	Material	1 in. th. H-T., 2 in. th. Mg.					1 in. th. H-T., 2 in. th. Mg.					1 in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	5.1	3.8	3.1	2.6	2.2	4.5	3.4	2.7	2.2	1.9	4.1	3.0	2.4	2.0	1.7
	Saving per yr.	3.78	5.13	6.47	7.79	9.13	4.35	5.88	7.39	8.93	10.44	4.85	6.54	8.23	9.93	11.62
Covering and application list − 20%	*Months Required*	4.1	3.1	2.5	2.1	1.8	3.6	2.7	2.2	1.8	1.5	3.3	2.4	2.0	1.6	1.4
	Saving per yr.	3.82	5.17	6.51	7.83	9.17	4.39	5.92	7.43	8.97	10.48	4.89	6.58	8.27	9.97	11.66
4 in. Pipe	Material	1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	4.4	3.3	2.6	2.2	1.9	3.8	2.9	2.3	1.9	1.6	3.4	2.5	2.0	1.7	1.5
	Saving per yr.	7.13	9.62	12.11	14.61	17.11	8.22	11.08	13.95	16.80	19.65	9.31	12.53	15.75	18.97	22.20
Covering and application list − 20%	*Months Required*	3.5	2.6	2.1	1.8	1.5	3.1	2.3	1.8	1.5	1.3	2.7	2.0	1.6	1.4	1.2
	Saving per yr.	7.20	9.69	12.18	14.68	17.18	8.29	11.15	14.02	16.87	19.72	9.38	12.61	15.83	19.04	22.27
6 in. Pipe	Material	1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	3.6	2.7	2.2	1.8	1.6	3.2	2.4	1.9	1.6	1.4	2.8	2.1	1.7	1.4	1.2
	Saving per yr.	10.47	14.09	17.72	20.37	24.97	12.10	16.28	20.47	24.65	28.80	13.79	18.55	23.27	28.00	32.77
Covering and application list − 20%	*Months Required*	2.9	2.2	1.7	1.5	1.2	2.5	1.9	1.5	1.3	1.1	2.2	1.7	1.3	1.1	1.0
	Saving per yr.	10.57	14.19	17.82	20.47	25.07	12.20	16.38	20.57	24.75	28.90	13.89	18.65	23.37	28.10	32.87
8 in. Pipe	Material	1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	3.0	2.2	1.8	1.5	1.3	2.6	1.9	1.5	1.3	1.1	2.3	1.7	1.4	1.1	1.0
	Saving per yr.	13.69	18.44	23.15	27.89	32.64	15.78	21.19	26.59	32.09	37.49	18.05	24.19	30.39	36.59	42.79
Covering and application list − 20%	*Months Required*	2.6	2.0	1.6	1.3	1.1	2.3	1.7	1.4	1.1	1.0	2.0	1.5	1.2	1.0	0.9
	Saving per yr.	13.79	18.54	23.25	27.99	32.74	15.88	21.29	26.69	32.19	37.59	18.15	24.29	30.49	36.69	42.89
10 in. Pipe	Material	1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	3.2	2.4	1.9	1.6	1.4	2.8	2.1	1.7	1.4	1.2	2.4	1.8	1.5	1.2	1.0
	Saving per yr.	17.05	22.40	28.80	34.70	40.50	19.60	26.35	33.10	39.85	46.60	22.50	30.20	37.90	45.60	53.30

TABLE V—*Continued*

Pipe Temperature °F.		800					850					900				
	Fuel Cost	.15	.20	.25	.30	.35	.15	.20	.25	.30	.35	.15	.20	.25	.30	.35
10 in. Pipe	Material	1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.					1½ in. th. H-T., 2 in. th. Mg.				
Covering and application list—20%	*Months Required*	2.5	1.9	1.5	1.3	1.1	2.2	1.6	1.3	1.1	0.9	1.9	1.4	1.2	1.0	0.8
	Saving per yr.	17.17	23.02	28.92	34.82	40.62	19.72	26.47	33.22	39.97	46.72	22.62	30.32	38.02	45.72	53.42
12 in. Pipe	Material	2 in. th. H-T., 2 in. th. Mg.					2 in. th. H-T., 2 in. th. Mg.					2 in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	3.5	2.6	2.1	1.8	1.5	3.1	2.3	1.8	1.5	1.3	2.7	2.0	1.6	1.4	1.2
	Saving per yr.	20.10	27.10	33.10	40.10	37.10	23.20	31.20	39.20	47.20	55.20	26.60	35.70	44.80	54.05	63.20
Covering and application list—20%	*Months Required*	2.8	2.1	1.7	1.4	1.2	2.5	1.8	1.5	1.2	1.1	2.2	1.6	1.3	1.1	0.9
	Saving per yr.	20.26	27.26	33.26	40.26	47.26	23.36	31.36	39.36	47.36	55.36	26.76	35.86	44.96	54.21	63.36
14 in. Pipe	Material	2 in. th. H-T., 2 in. th. Mg.					2 in. th. H-T., 2 in. th. Mg.					2 in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	3.4	2.6	2.0	1.7	1.5	3.0	2.3	1.8	1.5	1.3	2.6	2.0	1.6	1.3	1.1
	Saving per yr.	22.04	29.64	37.44	44.94	52.64	25.44	34.24	42.46	57.74	60.54	29.16	39.16	49.16	59.16	69.16
Covering and application list—20%	*Months Required*	2.8	2.1	1.7	1.4	1.2	2.4	1.8	1.4	1.2	1.0	2.1	1.6	1.3	1.1	0.9
	Saving per yr.	22.21	29.81	37.51	45.11	52.81	25.61	34.41	43.13	51.91	60.71	29.33	39.33	49.33	59.33	69.33
16 in. Pipe	Material	2 in. th. H-T., 2 in. th. Mg.					2 in. th. H-T., 2 in. th. Mg.					2 in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	3.4	2.5	2.0	1.7	1.4	2.9	2.2	1.8	1.5	1.3	2.6	1.9	1.5	1.3	1.1
	Saving per yr.	25.15	33.85	42.55	51.15	59.95	28.95	38.95	48.95	58.85	68.85	33.15	44.55	55.95	67.25	78.65
Covering and application list—20%	*Months Required*	2.7	2.0	1.6	1.3	1.2	2.3	1.8	1.4	1.2	1.0	2.0	1.5	1.2	1.0	0.9
	Saving per yr.	25.34	34.04	42.74	51.34	60.04	29.14	39.14	49.14	59.04	69.04	33.34	44.74	56.14	67.44	78.84
18 in. Pipe	Material	2 in. th. H-T., 2 in. th. Mg.					2 in. th. H-T., 2 in. th. Mg.					2 in. th. H-T., 2 in. th. Mg.				
Covering and application list	*Months Required*	3.2	2.4	1.9	1.6	1.4	2.8	2.1	1.7	1.4	1.2	2.5	1.8	1.5	1.2	1.1
	Saving per yr.	28.33	38.13	47.98	57.63	67.48	32.68	43.88	55.08	66.28	77.48	37.18	50.08	62.98	75.68	88.48
Covering and application list—20%	*Months Required*	2.6	1.9	1.5	1.3	1.1	2.2	1.7	1.3	1.1	1.0	2.0	1.5	1.2	1.0	0.8
	Saving per yr.	28.53	38.33	48.18	57.83	67.68	32.88	44.08	55.28	66.48	77.68	37.38	50.28	63.18	75.88	88.68
Flat Surface	Material	2 in. th. H-T., 2½ in. th. Mg.					2 in. th. H-T., 2½ in. th. Mg.					2 in. th. H-T., 2½ in. th. Mg.				
Covering and application list	*Months Required*	2.7	2.0	1.6	1.4	1.2	2.8	1.8	1.4	1.2	1.0	2.1	1.6	1.3	1.0	0.9
	Saving per yr.	5.76	7.73	9.72	11.72	13.70	6.61	8.88	11.14	13.40	15.67	7.57	10.15	12.72	15.32	17.88
Covering and application list—20%	*Months Required*	2.2	1.6	1.3	1.1	0.9	1.9	1.4	1.1	1.0	0.8	1.7	1.3	1.0	0.8	0.7
	Saving per yr.	5.80	7.77	9.76	11.76	13.74	6.65	8.92	11.18	13.44	15.71	7.61	10.19	12.76	15.36	17.92

pipes, painting, weight of canvas and application of canvas (pasted or stitched).

Before compiling Tables III, IV and V, the author corresponded with ten of the largest firms of consulting engineers in the power-plant field in regard to the cost of steam and specifications for thickness of material used as standard practice in insulating superheated steam lines. The cost of steam for these firms was found to vary from 14 to 50 cents per 1,000,000 B.T.U. The cost and application of the covering varies for different plants as mentioned above. However, one large pipe covering contractor finds for his work that in general the actual cost of covering for superheated steam lines to the central station in place and finished is approximately the list net price of the covering.

The price list of 85 per cent magnesia covering is shown in Table VI. This list is used in quoting prices on all types of covering on the market at present. The actual cost of any given type of insulation is quoted at so many points off the list price.

In order to form a definite comparison, the author has chosen for the cost of covering as applied, list net, and list−20 per cent and the cost of fuel at the boiler nozzle of 15, 20, 25, 30, and 35 cents per 1,000,000 B.T.U. There are many cases where the actual cost and application of pipe covering will exceed the list price of the covering and there are also many cases where the cost of steam will greatly exceed 35 cents per 1,000,000 B.T.U.

In order to make intelligent use of the tables shown it will be necessary for the engineer to first determine the cost of steam for his particular case and the approximate cost of the covering in terms of the list price. If these costs do not correspond with those given in the tables, it will be necessary to interpolate. As mentioned previously, however, the main object in presenting these tables is to convince the engineer of the large savings that can be accomplished by properly insulating superheated steam surfaces.

The tables show the time required to repay the original cost of the covering and its application, and also the savings in dollars per year per lineal foot of pipe and per sq. ft. of flat surface, for various temperatures and pipe sizes. In computing the tables "Hi-Temp" and 85 per cent magnesia have been used as the insulation. The most economical thickness has been used for the average of the steam costs assumed and the thickness of the "Hi-Temp" as the inner layer has been chosen so that the temperature at the inner

TABLE VI

Price Lists, Adopted August 1, 1907

85% Carbonate of Magnesia Pipe-Coverings, for Wrought Iron Pipes

Nominal Pipe Size	Thickness of Standard Covering	Price per Lineal Foot Canvas Jacketed	Thickness of Covering	Price per Lineal Foot Canvas Jacketed	Thickness of Covering	Price per Lineal Foot Canvas Jacketed	Double Layer Double Standard Thickness	Price per Lineal Foot Canvas Jacketed	Double Layer Total Thickness 3 Ins.	Price per Lineal Foot Canvas Jacketed
In.	In.		In.		In.		In.		In.	
1/2	7/8	$0.22	1 1/2	$0.46	2	$0.75	1 3/4	$0.65	3	$1.20
3/4	7/8	.24	1 1/2	.49	2	.80	1 3/4	.70	3	1.35
1	7/8	.27	1 1/2	.52	2	.85	1 3/4	.75	3	1.40
1 1/4	7/8	.30	1 1/2	.56	2	.90	1 3/4	.80	3	1.45
1 1/2	7/8	.33	1 1/2	.60	2	.95	1 3/4	.85	3	1.55
2	1 1/32	.36	1 1/2	.64	2	1.00	2 1/16	.90	3	1.65
2 1/2	1 1/32	.40	1 1/2	.70	2	1.05	2 1/16	1.00	3	1.75
3	1 1/32	.45	1 1/2	.76	2	1.15	2 1/16	1.10	3	1.90
3 1/2	1 1/32	.50	1 1/2	.82	2	1.25	2 1/16	1.20	3	2.05
4	1 1/8	.60	1 1/2	.88	2	1.35	2 1/4	1.40	3	2.20
4 1/2	1 1/8	.65	1 1/2	.94	2	1.45	2 1/4	1.50	3	2.35
5	1 1/8	.70	1 1/2	1.00	2	1.55	2 1/4	1.60	3	2.50
6	1 1/8	.80	1 1/2	1.10	2	1.70	2 1/4	1.80	3	2.70
7	1 1/4	1.00	1 1/2	1.20	2	1.85	2 1/2	2.25	3	2.90
8	1 1/4	1.10	1 1/2	1.35	2	2.00	2 1/2	2.50	3	3.15
9	1 1/4	1.20	1 1/2	1.50	2	2.20	2 1/2	2.70	3	3.40
10	1 1/4	1.30	1 1/2	1.65	2	2.40	2 1/2	2.90	3	3.65
*12	1 1/2	1.85	1 1/2	1.85	2	2.70	3	4.10	3	4.10
14	1 1/2	2.10	1 1/2	2.10	2	3.00	3	4.60	3	4.60
16	1 1/2	2.35	1 1/2	2.35	2	3.30	3	5.10	3	5.10
18	1 1/2	2.60	1 1/2	2.60	2	3.60	3	5.60	3	5.60
20	1 1/2	2.85	1 1/2	2.85	2	4.00	3	6.00	3	6.00
24	1 1/2	3.30	1 1/2	3.30	2	4.50	3	7.00	3	7.00
30	1 1/2	4.00	1 1/2	4.00	2	5.50	3	8.40	3	8.40

* All coverings larger than 10 inches furnished in segment form; jackets and bands not included.

Double standard thickness—the inner layer is furnished in sections for pipe sizes up to and including 10 inches, and in curved blocks for larger sizes. The outer layer is furnished in sections for pipe sizes up to and including 8 inches, and in curved blocks for larger sizes.

Double 1 1/2-inch thickness—the inner layer is furnished in sections for pipe sizes up to and including 10 inches, and in curved blocks for larger sizes. The outer layer is furnished in sections for pipe sizes up to and including 7 inches, and in curved blocks for larger sizes.

85% Carbonate of Magnesia Blocks, For Covering Boilers and Similar Surfaces

Thickness	Price per Sq. Ft.	Thickness	Price per Sq. Ft.	Thickness	Price per Sq. Ft.	Thickness	Price per Sq. Ft.
7/8 inch	$0.30	1 1/2 inch	$0.45	2 1/8 inch	$0.64	2 3/4 inch	$0.83
1 "	.30	1 5/8 "	.49	2 1/4 "	.68	2 7/8 "	.87
1 1/8 "	.34	1 3/4 "	.53	2 3/8 "	.72	3 "	.90
1 1/4 "	.38	1 7/8 "	.57	2 1/2 "	.75	3 1/4 "	.98
1 3/8 "	.42	2 "	.60	2 5/8 "	.79	3 1/2 "	1.05
						4 "	1.20

STANDARD BLOCK SIZES
6″ x 36″ 3″ x 18″

surface of the magnesia next to the "Hi-Temp" will not exceed 550° F.

The thicknesses used in these tables can safely be used for other insulations having approximately the same conductivity as "Hi-Temp" and magnesia and can be considered as standard practice for superheated steam temperatures, as they have been worked out on a scientific basis and also in accordance with the standard thicknesses of coverings as manufactured for the different pipe sizes.

It should be noted that the temperatures given are pipe temperature and not superheated steam temperatures. There has been considerable discussion lately on the temperature drop from the superheated steam to the wall of the pipe, some engineers maintaining that in certain cases the drop is considerably over 100 deg., while others say that it is only a few degrees. The author has made no study of this problem, but thinks that in most practical cases the drop is comparatively small. Recent practical tests by one large power plant gave only a few degrees drop.

In making the calculations, a room temperature of 70° F. has been assumed and the yearly fixed charges for the covering have been taken as 13 per cent of the cost of the covering applied (6 per cent interest, 5 per cent deterioration, 2 per cent miscellaneous).

To assist any one who desires to check these tables or who wishes to calculate the savings for some particular case of his own, an example is worked out showing the method used in determining the values given in the tables.

Determine the length of time required to pay for the installation and the saving per year per lineal foot length of pipe for a 12-inch pipe at a temperature of 700° F., when insulated with 1½ inches

of "Hi-Temp" and 2 inches of 85 per cent magnesia. The cost of steam at the boiler nozzle is assumed to be 35 cents per 1,000,000 B.T.U., the cost of the covering when applied is assumed as list net, and the room temperature is 70° F.

The heat loss through the insulation will be calculated first, because it is the most difficult part of the problem. In order to determine the heat loss through the insulation, it is necessary to know the temperatures at the inner and outer surfaces and the conductivity of the material at the mean temperature between the two surfaces. Since in this case only the pipe temperature and room temperature are known, it is necessary to determine the outer surface or canvas temperature. Probably the simplest procedure for calculating the heat loss through a compound covering is to make an assumption of the outer surface temperature and the temperature between the two types of insulation or at the outer surface of the "Hi-Temp" and the inner surface of the magnesia, then from the conductivity curves determine the conductivity of the materials at the mean of the surface temperatures assumed. The loss through the covering should then be calculated for the assumed outer temperature, and this loss should be checked against the loss as obtained by substitution in surface loss-equation (4).

If the two losses do not check, the assumed outer surface temperature and the assumed temperature at the junction of the two materials must be changed according to the indications of the calculation and the process repeated until the two losses or the outer surface temperatures check.

The equation for compound sections on a cylindrical surface in terms of heat loss per square foot of outer surface is

$$h = \frac{T_1 - T_2}{\dfrac{r_s \log_e \dfrac{r_2}{r_1}}{K_1} + \dfrac{r_s \log_e \dfrac{r_s}{r_2}}{K_2}} \tag{5}$$

in which

T_1 = temperature at inner surface of insulation,
T_2 = temperature at outer surface of insulation,
r_s = radius of outer surface of insulation,
r_1 = radius of inner surface of insulation,
r_2 = radius between first and second layer of insulation,
K_1 = thermal conductivity of first layer of insulation,
K_2 = thermal conductivity of second layer of insulation.

For a 12-inch pipe

$$r_1 = 6.375, \qquad r_2 = 7.875, \qquad r_s = 9.875,$$

$$r_s \log_e \frac{r_2}{r_1} = 2.09,$$

$$r_s \log_e \frac{r_s}{r_2} = 2.23.$$

First, a canvas temperature of 125° F. is assumed. The total drop in temperature through the two coverings then is 700° − 125° = 575° F. The next step is to assume the temperature drop through each insulation, in order to determine the conductivity value to use. No rule can be given for the first assumption; but it will be found that the second assumption can be calculated fairly closely. It is seen from the conductivity curves in Fig. 2 that the conductivity of "Hi-Temp" is higher than that of magnesia, but the material which is applied next to the pipe is more effective than the second layer of material, other things being equal, so there is first assumed a drop of 250° F. through "Hi-Temp" with the remaining drop of 325° F. through magnesia. The temperature between the "Hi-Temp" and the magnesia covering then is 700° − 250° = 450° F.

The mean temperature of "Hi-Temp" is

$$\frac{700° + 450°}{2} = 575° \text{ F.},$$

and from Fig. 2, $K_1 = 0.651$. The mean temperature of magnesia is

$$\frac{450° + 125°}{2} = 287.5° \text{ F.},$$

and $K_2 = 0.502$.

Substituting the values obtained above in equation 5,

$$h = \frac{700 - 125}{\frac{2.09}{0.651} + \frac{2.23}{0.502}} = \frac{575}{3.21 + 4.45} = 75.1 \text{ B.T.U.}$$

Substituting this value in the surface-loss equation and obtaining by interpolation the value of 320 for $\frac{564}{19.75^{0.19}}$ from Table I,

$$Td = \frac{272.5 \times 75.1}{75.1 + 320} = 51.7.$$

This indicates that the 55° F. temperature difference first chosen was too high, and there is next assumed a temperature difference of 52° F., or a canvas temperature of 122° F., since the canvas temperature will generally be fairly close to the canvas temperature first obtained by substituting in the surface-loss equation.

The temperature drop through "Hi-Temp" for the foregoing calculation was approximately 3.21×75.1, or 241° F. Since there has been assumed a canvas temperature decrease of 3° F., there will be assumed a corresponding increase in the drop through the covering, or the temperature drop through "Hi-Temp" as 242° F., and the drop through magnesia as 336° F., with the temperature between the "Hi-Temp" and magnesia covering as 458° F.

The mean temperature of "Hi-Temp" then is

$$\frac{700^\circ + 458^\circ}{2} = 579^\circ \text{ F.},$$

and $K_1 = 0.652$. The mean temperature of the magnesia covering is

$$\frac{458^\circ + 122^\circ}{2} = 290^\circ \text{ F.},$$

and $K_2 = 0.503$. Then

$$h = \frac{578}{\frac{2.09}{0.652} + \frac{2.23}{0.503}} = \frac{578}{3.21 + 4.44} = 75.5 \text{ B.T.U.}$$

Checking again for the canvas temperature difference,

$$Td = \frac{272.5 \times 75.5}{75.5 + 320} = 52^\circ \text{ F.}$$

This value checks with the last value of 52° F. assumed; also the drop through the "Hi-Temp" $= 3.25 \times 75.5 = 242$, which checks with the value last assumed, and the heat loss is 75.5 B.T.U.

The total heat loss per square foot of pipe surface per hour is then

$$75.5 \times \frac{9.875}{6.375} = 116.8 \text{ B.T.U.}$$

From Fig. 1 the heat loss from a bare 12-inch pipe at 630° F. temperature difference $= 630 \times 5.74 = 3617$ B.T.U. The saving then $= 3617 - 117 = 3500$ B.T.U. per square foot of pipe surface per hour. The saving per lineal foot length of pipe $= 3500 \times 3.344$

= 11,700 B.T.U. per hour. With the cost of steam at 35 cents per 1,000,000 B.T.U., the saving in dollars per year

$$= \frac{11{,}700 \times 8760 \times 0.35}{1{,}000{,}000} = 36.05.$$

From Table VI the list price of 1.5-inch "Hi-Temp" and 2-inch magnesia on 12-inch pipe = $5.00. The annual fixed charges have been assumed as 13 per cent of the cost of covering and application, or, in this case, 13 per cent of list net = 5.00 × 0.13 = 0.65.

The net annual saving then = 36.05 − 0.65 = $35.40 per foot length of pipe. The time required to repay the original cost of the installation

$$= \frac{12 \times 5.00}{36.05} = 1.66 \text{ months,}$$

or approximately 50 days.

TABLE VII

COST OF STEAM PER 1,000,000 B.T.U.

Boiler Efficiency %	Coal			Oil			Natural Gas			Artificial Gas		
	Cost per ton 2000 lbs.			Cost per barrel 327 lbs.			Cost per 1000 cu. ft.			Cost per 1000 cu. ft.		
	$3.00	$4.00	$5.00	$1.00	$1.25	$1.50	$0.40	$0.50	$0.60	$1.00	$1.25	$1.50
50.....	0.23	0.31	0.38	0.32	0.40	0.48	0.80	1.00	1.20	3.33	4.16	5.00
60.....	0.19	0.26	0.32	0.27	0.34	0.40	0.67	0.83	1.00	2.78	3.47	4.17
70.....	0.16	0.22	0.27	0.23	0.29	0.34	0.57	0.71	0.86	2.38	2.98	3.57
80.....	0.14	0.19	0.24	0.20	0.25	0.30	0.50	0.62	0.75	2.08	2.60	3.12
90.....	0.13	0.17	0.21	0.18	0.22	0.27	0.44	0.55	0.67	1.85	2.31	2.78

Table VII gives the cost of steam per 1,000,000 B.T.U. for various types of fuel at various costs and when burned under various boiler efficiencies. In compiling this table the heat content of coal has been taken as 13,000 B.T.U. per lb., fuel oil at 19,000 B.T.U. per lb. (327 lbs. per barrel), natural gas at 1000 B.T.U. per cu. ft., and artificial gas at 600 B.T.U. per cu. ft.

By the aid of the tables and curves presented in this paper it is hoped that any one concerned with the conservation of fuel will be able to determine just what saving can be effected under any given condition. While the tables show the savings in terms of

dollars and cents and in terms of the time required to repay the original cost of the investment, they can readily be transferred to tons of coal, barrels of oil, etc.

Impressing the individual with the savings to be effected in dollars and cents will more readily convince him of the value of the savings in terms of coal or gas and thus help to conserve the rapidly diminishing natural fuel resources of this country.

Discussion

Mr. Heilman [before reading paper]: The title of my paper should be "Insulation of Superheated Steam Surfaces." I want to try to bring before the body here the insulation of high temperature surfaces, because it is a well-known field. It is a well-known fact that temperatures are increasing daily, and where we had temperatures in ordinary power plants a few years ago at 550 degrees, we are now up to 750 or 800 degrees, and in chemical processes we have temperatures up to 900 and even up to 1,100 degrees Fahrenheit.

THE SOLID PHASES DEVELOPED IN BOILER WATERS[1]

By RALPH E. HALL[2] and H. E. MERWIN[3]

Read at the Pittsburgh Meeting, December 4, 1924

Practically all natural waters contain mineral ingredients; and these, according to the use made of a water, may be of benefit or detriment. It is the purpose of this article to trace the solid phase development when natural fresh waters are evaporated under steam boiler conditions, and to indicate a control over such development satisfactory for the continuous production of steam.

Relation Between the Use For A Water and Control of Solid Phases

The industrial uses of water may be divided into two classes: (*a*) those in which change in state of the water is of negligible amount, and (*b*) those in which it is the essential requisite. As an example of the former, the use of water for laundry purposes may be cited; of the latter, its use in the manufacture of artificial ice, or the production of steam.

In Table I are presented analyses of a number of natural waters, chosen without reference to their source, but with the purpose of illustrating variations in concentration which may occur in two components in particular—SO_4 and HCO_3—though it is noticeable that the total concentration of calcium and magnesium follows closely the total concentration of negative radical in the waters.

If waters such as these are to be used for laundry purposes, it is essential that the calcium, magnesium, and iron content be reduced as far as possible for economy in soap consumption and because of trouble induced by the insoluble substances formed. Any treatment in excess of chemical equivalence must be based upon the allowable alkalinity in waters used for this purpose.

[1] Published by permission of the Director, U. S. Bureau of Mines. This article presents results obtained in a cooperative investigation of the Bureau of Mines and the Hagan Corporation of Pittsburgh, Pa.

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TABLE I

COMPOSITION OF THE MINERAL INGREDIENTS IN VARIOUS NATURAL WATERS (PARTS PER MILLION)

No.	Source	SiO_2	Fe	Ca	Mg	Na	HCO_3	Cl	SO_4	Free H_2SO_4
1*	Coal mine drainage	32	62	234	110	133	—	Tr	1562	203
2	Youghiogheny River, McKeesport, Pa.	25	41	109	22	149	—	20	720	69
3†	Missouri River, Kansas City, Kan.	37	0.7	62	18	44	202	13	135	—
4	City Water, Flint, Michigan	3	3	68	27	22	275	15	81	—
5	Ohio River, Woodlawn, Pa.	2	0.4	22	5	17	20	14	76	—
6	Canal, Rumford, Maine	1	2	3	1	2	5	3	6	—
7†	Hudson River, Hudson, New York	11	0.2	21	4	8	73	4	16	—
8†	Lake Erie, Buffalo, N. Y.	6	0.1	31	8	7	114	9	13	CO_3 3
9	City Water, Washington, Pa.	6	3	44	5	16	81	26	60	—
10	Well, Washington, Pa.	29	5	98	16	198	654	52	128	—
11	Mine water, Wilton, N. D.	15	2	569	254	26	506	21	1996	—

* Bulletin 4, Coal-Mining Investigations, Carnegie Institute of Technology (1922).

† Water-Supply Paper 274, U. S. Geological Survey (1911). Other analyses by Grace Thomas, Hagan Corporation.

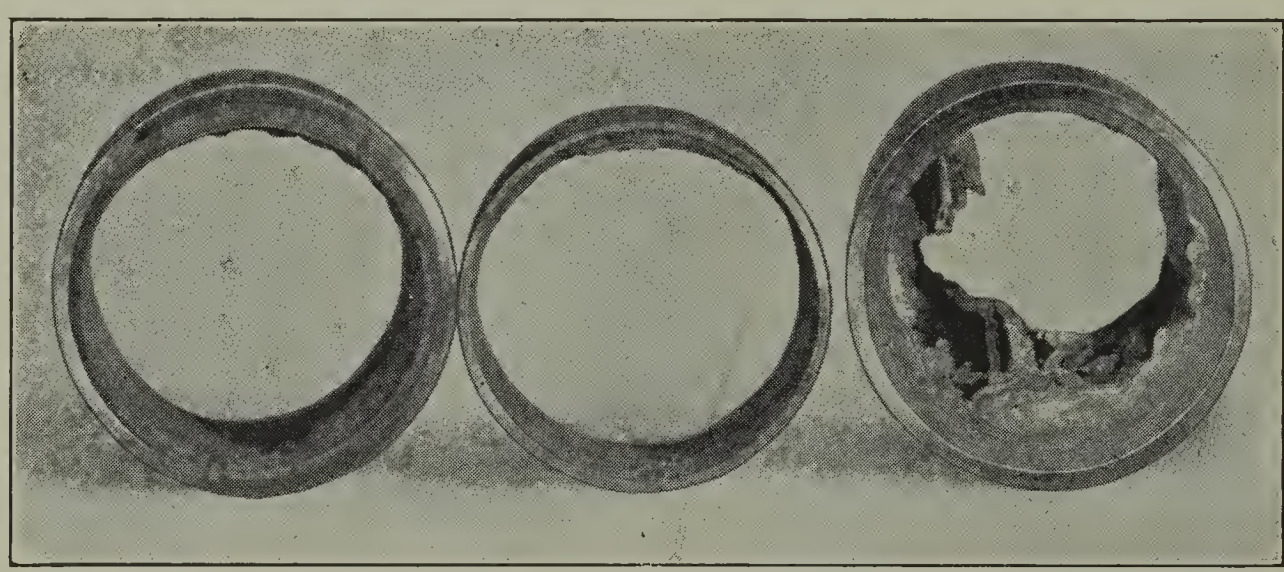


FIG. 1. Boiler Scale on Tubes from the Evaporation of Water

There are several points in common in the manufacture of artificial ice and the generation of steam. Change in the heat content of water is effected through metal surfaces which therefore should be maintained clean. The concentration of soluble ingredients in the water phase increases as ice or steam is formed, and the blow-down of a boiler is analogous to replacing the concentrated water with more dilute when freezing is nearing completion.

But whereas, in the formation of ice the metal surfaces are colder than the water, are maintained at a uniform temperature, and never are in contact with a concentrated water because protected by the solid phase forming, in boilers operating at different pressures the concentrated water is subjected to a temperature range extending to 225° C. or higher and is continually in contact with the evaporating surfaces. At them, also, the steam forms thus favoring deposition of insoluble solids upon them.

Because the boiler waters in different boilers are not maintained at the same temperature and because they are continually in contact with the evaporating surfaces, treatment of the water for preventing solid-phase deposition upon them becomes a function of the operating pressure of the boiler and the concentration of certain components in the boiler water. Thus it is apparent that a treatment, applied to waters such as those of Table I, which is entirely satisfactory for laundry purposes or ice manufacture, may fail in preventing scale formation when applied to boiler feed water; and the treatment successful for a boiler operating at one pressure, is only by chance fully satisfactory at a different pressure.

Solid Phases Resulting From Evaporating Natural Waters

Since the aim of boiler-water treatment is to prevent the deposition of solid phase as adherent scale, it is essential to know the characteristics of various boiler scales, and the types of water evaporated in forming them. In Table II, such information is assembled for a number of typical scales. Column 2 presents the type of water in Table I which was used as feed water; column 3, the type of scale and its location in the boiler. Columns 4–12 give the results of chemical analysis, and column 13 the actual chemical substance which comprises the major portion of the scale as determined by the petrographic microscope. Fig. 1 shows a characteristic condition of boiler tubes, when evaporating a water similar to No. 5 (Table I): Fig. 2, the steam drum, after evaporation of 58,334,000 lbs. of the same type of water.

Nos. 7 and 9 (Table II), aragonite and calcite, respectively, are soft adherent scales deposited by the feed water before concentration in the boiler, and on surfaces at which no evaporation was occurring. No. 8 represents the sludge forming simultaneously with

TABLE II

SOLID PHASES RESULTING FROM EVAPORATING NATURAL WATERS AT BOILER PRESSURES WITHOUT TREATMENT OR WITH PARTIAL TREATMENT. (ANALYSES REPORTED IN PER CENT.)

1	2	3	4	5	6	7	8	9	10	11	12	13
No.	Type of water evaporated. No. in Table 1	Type of scale and location in boiler	SiO_2	Fe_2O_3	CaO	MgO	Na_2O	SO_3	CO_2	Loss at 105°	Net ignition loss	Microscopical analysis
1	Nos. 5 and 7	Hard adherent on tubes	2.3	0.8	38.5	2.6	—	54.1	—	0.1	1.9	Practically pure anhydrite
2	No. 5 or 7	Hard adherent on drum	1.5	1.5	38.3	2.9	1.8	50.8	0.7	0.3	2.0	Practically pure anhydrite
3	No. 5. Partial treatment	Hard adherent on tubes	6.0	4.2	31.8	9.2	—	43.3	0.2	—	6.6	Anhydrite and isotropic material which is probably hydrous magnesium silicate
4	Mixture of Nos. 9 and 10. No treatment	Sludge and broken scale from mud drum of Stirling boiler before turbining	6.9	1.3	40.8	12.8	—	1.6	31.2	0.7	5.5	Loose material-calcite. The hard scales or flakes contain much isotropic, light brownish material, which is probably hydrous magnesium silicate. (N = 1.53–1.54)
5	do	Hard adherent on front tubes of Stirling boiler	9.7	1.7	29.1	24.2	—	0.8	22.7	1.5	10.1	Calcite, brucite, hydrous magnesium silicate (as above)
6	do	Hard adherent on steam drum of Stirling boiler	17.1	1.8	26.1	22.8	—	0.9	20.2	1.6	9.4	Calcite; hydrous magnesium silicate (as above)

TABLE II *Continued*

1	2	3	4	5	6	7	8	9	10	11	12	13
No.	Type of water evaporated. No. in Table 1	Type of scale and location in boiler	SiO_2	Fe_2O_3	CaO	MgO	Na_2O	SO_3	CO_2	Loss at 105°	Net ignition loss	Microscopical analysis
7	do	Soft adherent from top of rear bank of tubes (Stirling boiler)	1.5	0.9	52.9	1.8	—	0.8	40.1	0.1	2.0	Aragonite
8	do	Sludge from bottom of mud pan, Stirling boiler	0.7	1.2	51.1	3.7	—	0.4	42.1	0.1	1.0	Calcite
9	No. 5 full treatment	Soft adherent on feed lines to boiler after heater	0.6	0.9	54.5	1.4	—	0.1	42.3	0	0.7	Calcite
10	No. 4 but lower in sulphate; partial treatment	No record; but probably from tubes	10.4	1.2	22.1	35.0	—	0.2	17.1	0.5	13.9	Calcite, brucite, hydrous magnesium silicate (as above)
11	Fully treated water	Hard adherent on tubes	45.4	6.9	32.9	1.8	6.7	0.7	2.1	1.4	2.0	A little anhydrite; isotropic material, presumably $CaSiO_3$
12			30.4	0.5	32.9	7.8	—	0	16.7	3.1	8.6	Apparently not a consolidated scale. Well formed calcite crystals are loose in a matrix of much smaller isotropic grains, the retractive indices of which indicate hydrous calcium and magnesium silicates
13	Partially treated water	Soft adherent on steam drum	12.0	1.4	30.7	17.5	—	14.4	15.5	1.0	8.5	

Chemical analyses by Grace Thomas, Hagan Corporation

the deposition of No. 7. The unstable aragonite [4] crystallized from a water with no treatment, while stable calcite developed as a sludge in the same waters and as scale from a water fully treated with lime and soda ash. However, in every scale from the evaporating surfaces thus far examined in which calcium carbonate was present, it has been in the form of calcite.

With the exception of the loose material in No. 4, which formed as a sludge in the boiler water, the remaining samples represent deposition at and on the evaporating surfaces. When a sulphate water such as Nos. 5 or 7 (Table I) is evaporated with no treatment, practically pure anhydrite results as in Nos. 1 and 2. If partial treatment is given, anhydrite may remain, and hydrous magnesium silicate appear as in No. 3; or, in case of higher bicarbonate content in the feed water (No. 4, Table I) and probably more nearly complete treatment, anhydrite may be entirely lacking, and calcite, brucite [$Mg(OH)_2$] and hydrous magnesium silicate form the scale, as in No. 10. This was practically the condition under which Nos. 4, 5 and 6 formed; for while no treatment was given the feed water, No. 10 (Table I) in its natural state contains sodium bicarbonate. The calcium silicate of No. 11 may be attributed to the fact that the feed water, heavily treated with alkali, was filtered hot through a sand filter. The conditions surrounding the formation of No. 12 are not known; but it is of importance in showing that calcite was not the material binding the scale, since its crystals were loose in a matrix of calcium and magnesium silicates.

Different Methods of Controlling Adherent Scale Growth

The mechanism of deposition of the soft adherent scales found in feed lines and composed mainly of calcite and aragonite has been considered elsewhere and methods of control and elimination have been discussed.[5] Attention will be given in this article only to the hard adherent scales deposited on evaporating surfaces. For the control of adherent scale development, the two general methods in vogue, and basically different in principle, will be discussed.

[4] Johnston J., Merwin, H. E., and Williamson, E. D., "The Several Forms of Calcium Carbonate," *Amer. J. Sci.*, vol. 41, 1916, pp. 473–515. The authors discuss the conditions which determine the crystallization of calcium carbonate as aragonite or calcite.

[5] Hall, Ralph E., "A System of Boiler Water Treatment Based on Chemical Equilibrium," *Jour. Ind. Eng. Chem.*, vol. 17, 1925, pp. 283–290. Ibid., "Water Treatment for Continuous Steam Production," *Mechanical Engineering*, vol. 46, 1924, pp. 810–17.

Treatment by Boiler Compounds

The principle underlying this type of treatment is that without reference to their composition the solid phases developed during the evaporation of natural waters may be made non-adherent (*a*) by the use of organic matter, whether such organic matter functions because of colloidal properties [6] or by reason of its influence on the crystalline character of the precipitate; [7] (*b*) by the development of finely divided precipitates which, in flocculating, carry with them all particles which would form adherent scale. In either case for successful results it is obvious that precipitation of solid phase must occur as distinct, individual crystals, or particles, free to move throughout the mass of the boiler water. Likewise, it is just as obvious that the hydroxide, carbonate, silicate or phosphate of soda, which a great many boiler compounds contain associated with their organic content need not be chemically equivalent to the scale forming materials in the boiler water, and as a limiting case, need not be used at all.

Treatment by Inorganic Chemicals

Two phases in the use of inorganic chemicals must be noted. In external application, as by the base exchange or lime-soda process, the quantity of chemical used in treatment is chemically equivalent to the scale-forming ingredients in the water, or slightly in excess of this amount. The underlying principle has been the removal of "scale-forming ingredients," so far as possible. Internal treatment with soda ash or sodium phosphate, etc., has been based on chemical equivalence of the "scale forming ingredients" intentionally in some cases; usually, however, the condition of the boiler at times of opening has been used as a guide for proportioning the chemical introduced during the following period of operation.

Treatment Based on the Principles of Chemical Equilibrium

It has been the function of this investigation to study intensively the mechanism of boiler scale formation, and to define conditions in the boiler water which if maintained, successfully prevent the

[6] Partridge, E. M., "The Sphere of Boiler Compounds—Colloid Chemistry and Scale Prevention," *Power*, vol. 60, 1924, pp. 56–60, Alexander, Jerome, Roger's Manual of Industrial Chemistry, 3d ed., p. 1149.

[7] French, D. K., "Internal Treatment of Boiler Water—Proper and Improper," *J. Ind. Eng. Chem.*, vol. 15 (1923), pp. 1239–1242.

growth of adherent scale on the evaporating surfaces under differentoperating conditions. The results may be summarized as follows:

A. The deposition responsible for the growth of adherent scale occurs mainly *in situ*, on evaporating surfaces, so that the crystals composing it, except those lodging incidentally in the matrix of the truly adherent material, never exist as individuals throughout the boiler water.

B. If S represents solubility and T temperature, then when dS/dT is positive for the solid phase precipitating deposition occurs mainly in the body of water, and no growth of adherent scale occurs on the evaporating surfaces; but if dS/dT is negative, a growth of adherent scale results.

C. The elimination of adherent scale growth, therefore, is attained by so adjusting concentrations in the boiler water that dS/dT for the solid phases in equilibrium is positive. This means that the concentration of treating chemical in the boiler water must be adjusted in accordance with the operating pressure of the boiler, and the concentration of unfavorable radical, usually sulphate. The point at which it is introduced, whether into boiler, or feed water, is a matter of indifference for this purpose.

Evidence upon which these conclusions are based may be summarized as follows:

A. Adherent scale is deposited *in situ*. The data of Table III were obtained in a chemical balance run on a 545 hp. Heine boiler for which the make-up water was 100 per cent, and no treatment whatever was used. The feed water was analogous to that of No. 5, Table I. In Table V, No. 5 is the analysis of the scale deposited, and Nos. 1 and 2 those of the sludges of blow-down and wash-back,[8] respectively.

Although many pounds of sulphate scale was depositing every 24 hours, it is notable that the amount of suspended matter in the boiler water was slight in amount, and that the constituents removed as solids in blow-down and wash-back were in different proportions from those in the scale forming and were of small weight. The distribution of calcium sulphate over the entire period was as follows:

[8] A filter was attached to the boiler through which boiler water was passing at a rate about one-fourth of the rate at which feed water was entering. It was washed back at regular intervals, and the sludge collected.

TABLE III

CHEMICAL BALANCE ON 545-HP. HEINE BOILER

Operating pressure: 150 lb. gage.
Water heating surface: 5,450 sq. ft.
Water in boiler: 34,800 lbs.
Feed water: South Pittsburgh filtered (Monongahela River) water.

Date	Total Feed Water. M lb.	Total Blow-down and Moisture in Steam M lb.	Suspended Matter in Boiler Water Parts per Million	Total Insoluble Solids Removed by Blow-down and Wash-back, lb.	Total Insoluble Solids Accumulating in Boiler as Adherent Scale, lb.
6/17/22	144.1	22.1	22	3.3	5.2
18	172.5	9.5	—	1.7	20.2
19	295.7	19.7	20	4.8	33.3
20	280.1	22.1	10	5.9	28.0
21	354.0	22.0	9	3.2	42.8
22	313.6	20.6	7	3.8	38.4
23	292.3	21.3	10	4.0	37.4
24	120.6	18.6	7	(4.0)*	7.8
25	8.6	8.6	—	(1.5)	−4.3
26	279.0	19.0	13	(4.0)	32.7
27	361.3	21.3	13	(2.0)	49.5
28	160.3	20.3	10	(2.0)	16.7
29	255.3	22.3	16	(2.0)	35.7
30	249.9	20.9	14	(2.0)	33.1
7/ 1/22	135.9	20.9	13	(2.0)	11.1
2	10.0	10.0	—	(2.0)	1.2
3	181.9	18.9	9	(2.0)	26.2
4	10.2	10.2	—	(2.0)	−5.9
5	300.2	20.2	19	(2.0)	45.8
6	245.1	21.1	16	(2.0)	21.4
7	281.9	21.9	16	1.9	28.2
8	177.1	21.1	11	1.4	13.0
9	10.2	10.2	—	(1.6)	−2.6
10	274.4	21.4	17	(1.6)	34.5
11	261.3	23.3	14	(1.6)	30.7
12	299.5	23.5	9	1.6	34.4
13	295.1	24.1	14	(1.6)	40.2
14	356.2	25.2	—	1.4	43.2
15	128.6	14.6	—	1.8	9.9
16	11.7	11.7	—	1.5	−6.1
17	282.4	19.4	—	2.2	44.5
18	378.8	26.8	—	1.2	56.9
19	327.6	27.6	—	0.8	43.8
20	366.4	26.4	—	3.1	46.5
21	358.0	26.0	—	3.2	48.3
					Total, 941.7

* The numbers in parentheses are estimated. Possible errors are of trifling significance in view of the values in column 6.

DISTRIBUTION OF CALCIUM SULPHATE

	Per Cent
Removed in blow-down and wash-back sludge	3.2
Removed in blow-down water	7.7
Deposited *in situ* as adherent scale	89.1

TABLE IV

RESULTS FOLLOWING PARTIAL TREATMENT

Other conditions the same as for Table III.

Date	Water Evaporated M lb.	Solids		Treatment
		Wash-back lb.	Blow-down lb.	Sodium Silicate lb.
7/24/22	257	0.2	0.3	None
25	265	1.0	0.5	App. 15
26	259	2.4	0.4	do
27	301	6.6	1.0	do
28	288	4.4	0.8	do
29	107	0.5	0.2	None
31	263	0.4	0.7	do
8/ 1/22	270	1.3	4.9	App. 15
2	463	4.7	0.6	do
3	55	1.9	0.2	do
				Soda Ash
8/29/22	200	7.3	—	50–60
30	234	6.5	3.0	do
31	218	10.0	8.2	do
9/ 1/22	109	11.7	12.7	do
10/10/22	—	10.4	—	do
11	460	11.2	29.6	do
12	515	13.6	33.4	do
13	—	13.3	27.6	do
14*	—	6.7	26.7	—
17	470	26.8	52.5	do
18	497	26.8	39.1	do
19	445	32.9	30.6	do

* Saturday a.m. only.

In Table IV are presented data obtained from the same boiler, when partial treatment was given the feed water. The ordinary commercial solution of silicate of soda was used first, to find if the finely divided precipitate, with its excellent flocculating characteristics, would not largely decrease the amount of calcium sulphate going into adherent scale. A voluminous precipitate was present in the boiler water, and what appeared to be a large quantity of material was retained by the filter and was present in the water from blow-down; but when it had been deprived of water, its

weight was small, as shown by the figures of columns 3 and 4 for silicate treatment. The analyses of sludge in blow-down and wash-back for August 27 are shown in Table IV (No. 3 and 4). The characteristic action of sodium silicate in loosening sulphate scale is evidenced by the broken scale in the sludge from blow-down on that date; the extremely high proportion of silica and magnesia in the sludge from the wash-back, in conjunction with the almost total absence of lime and SO_3 is evidence that the rather high lime and SO_3 content in the sludge from blow-down is due to broken scale, and not to the processes of flocculation or absorption. In any event, the decrease in rate of adherent scale formation was too small to be of material value.

In the second part of Table IV, the results attending the internal use of soda ash are given. The figures of column 5, representing the amount of soda ash used, are uncertain, except for October 17–19, when trouble with the chemical feed-pump had been eradicated; however, they represent the maximum amount used when no trouble developed. The test in October was made during the dry spell of 1922, when the feed water contained 70–80 parts per million of calcium. The amount of soda ash used was far less than chemically equivalent to the calcium content; and the feed water, entering the mud drum and attaining boiler water temperature, was supersaturated with calcium sulphate, and deposited this excess as loose crystals.[9] Probably some of this material was included in the solids noted, as evidenced by the extremely high weight of solids in blow-down and wash-back for October 17–19.

The loose sludge and thin scale developed when full internal treatment on the basis of chemical equilibrium was employed are Nos. 6, 7, and 8, Table V. The sulphate content of both sludge and scale had almost disappeared; simultaneously the amount of suspended material in the boiler water had increased.[10] In place of calcium sulphate crystallizing on the evaporating surfaces, calcium carbonate was precipitating as non-adherent particles. The thin scale does not increase in thickness, as long as its content of calcium sulphate and magnesium silicate remains small; but, as indicated by No. 13, Table I, the conditions suitable for their deposition in

[9] See reference 5.

[10] Hall, R. E., Fischer, Carl, and Smith, G. W., "The Prevention of Scale Formation by Boiler Water Conditioning," *Iron and Steel Engineer*, vol. 1, 1924. pp. 312–327.

quantity favor the growth of adherent scale which increases in thickness with continued evaporation.

TABLE V

ANALYSES OF SLUDGE AND SCALE FORMED IN BOILER (PER CENT)

No.	Sample from	Date Taken	SiO_2	Fe_2O_3 Al_2O_3	CaO	MgO	Na_2O	SO_3	CO_2	Moisture at 105°	Net Ignition Loss
1	Sludge in blowdown. No treatment	6/16/22	12.7	25.3	13.8	10.6	0.6	19.3	0	1.0	15.1
2	Sludge in wash-back. No treatment	6/16/22	11.4	22.2	12.9	15.3	2.1	19.0	—	0.7	19.3
3*	Sludge in blowdown, partial treatment with sodium silicate	7/27/22	7.1	13.3	29.4	3.5	Not determined	40.4	—	0.1	2.4
4	Sludge in wash-back, partial treatment with sodium silicate	7/27/22	37.1	15.9	1.4	20.0	do	1.5	—	5.8	18.0
5	Scale from tube surface	10/10/22	1.5	2.2	38.6	1.6	do	54.5	—	0.5	1.5
6	Thin scale on steam drum, full treatment with soda ash	12/ 9/23	4.6	12.9	37.6	6.2	—	1.3	34.9	0.1	3.1
7	Thin scale on tubes, full treatment with soda ash	12/ 9/23	2.2	3.4	49.9	3.0	—	2.2	38.3	0.1	1.3
8	Wash-back sludge, full treatment with soda ash	12/12/23	6.1	4.3	39.1	9.0	—	0.7	30.4	0.3	9.9

* Much broken scale in this sample.

It is apparent from this discussion that we believe the growth of adherent scale to result mainly from the deposition of calcium sulphate or calcium and magnesium silicates *in situ* on the evaporating surfaces. Crystallization to the limit of their solubility at boiler water temperatures occurs as unattached particles, as demonstrated for calcium sulphate [11] when its concentration in the feed water was high, and for magnesium silicate by the sludge formed in part treatment with sodium silicate (No. 4, Table V). The residual

[11] See reference 5.

salt in solution, deposited as evaporation occurs, is responsible for the growth of adherent scale. In such scale, crystal growth takes place usually with the formation of elongate crystals growing radially. Particles lodging as a sediment would not be thus regular, nor could the regularity observed in sections of scale be attained by unattached particles lodging incidentally, and remaining fast.

B. Relation Between Slope of Solubility Curve and Adherent Scale Growth

The thin layer of water directly in contact with the evaporating surface must represent the highest temperature in the boiler water for any cross section of a boiler tube in operation. Any substance in the boiler water, therefore, whose solubility decreases as temperature increases, tends to become supersaturated in this layer, and to crystallize at the heated surface. If solubility increases with temperature increase, deposition is not favored at the heated surface, but in the area of slightly lower temperature. Thus it is that calcium sulphate, the slope of whose solubility curve is negative, deposits largely as adherent scale; and that calcium carbonate, with dS/dT positive, precipitates mainly as non-adherent particles. The application of this principle to other salts has been discussed elsewhere.[12] It is interesting to note that in the evaporation on large scale of a natural brine at atmospheric pressure by live steam, crystals of sodium chloride form at the surface of the liquor and on the cool side-walls, but the hard scale on the heating coils is practically pure anhydrite. Data regarding the slopes of the solubility curves of hydrous calcium and magnesium silicate are not available; but the frequent appearance of the latter especially in quantity in hard adherent scales is indicative of a negative sign.

The reason for the growth of scale composed of substances with dS/dT negative seems definite. Why a thin coating of carbonate scale should form on the evaporating surfaces, but not increase in thickness, when the proper equilibrium relations are maintained, is puzzling. At one time we thought rapid decomposition of the excess carbonate radical at the heated surface might develop a sufficiently high hydroxyl concentration to cause the deposition of calcium hydroxide,[13] for which dS/dT is negative, and which later

[12] See reference 5.

[13] See reference 10.

might change to carbonate. Failure by microscopic examination to find any calcium hydroxide in such scales, or any evidence pointing to a change from hydroxide to carbonate, proves that this is not the mechanism of formation. It is noticeable, however, that isotropic magnesium silicate is always present in these thin scales; and its ability to function in causing adherent scale growth is well shown by scales No. 3, 4, 5, 6, and 10, Table II. The primary formation perhaps may be due to the fact that while the sign of the dS/dT relation defines the point of crystallization to a large degree, it does not hold with complete exactness, and any departure therefrom would be emphasized by high rate of evaporation. A balance of conditions probably dictates the thickness which the thin scale attains. Carbonate radical decomposition at the heated surface increases the solubility of calcium carbonate locally because of decrease in common ion effect. The thin carbonate scale tends to remain relatively porous and friable, and therefore more subject to erosion than anhydrite scale, which is comparatively very impervious to penetration by water. We know, however, that erosion does not play an important rôle in the steam drum; for scratches made in such a coating with the fingers more than a year ago, are still plainly apparent, after the evaporation of more than 120 million lbs. of water. The porosity of the carbonate scale gives ample opportunity for anhydrite or magnesium silicate to crystallize in the interstices, thus strengthening the structure, and causing a thicker scale to build readily. Hence it is that if the solid phase in equilibrium with the boiler water is not continually controlled, an adherent scale which increases in thickness is built on the evaporating surfaces. While, practically, it is impossible to prevent entirely the presence of magnesium silicate in the carbonate coating, its amount can be held low and sulphate can be almost completely eliminated.

C. Conditions for Preventing Growth of Adherent Scale

Maintenance of definite conditions in the boiler water is essential to the control of the solid phase in equilibrium. "Favorable" substances may be defined as those which precipitate as individual unattached particles in the boiler water, and "unfavorable" substances as those which form adherent scale. Since the slopes of their solubility curves are opposite in sign, the curves are divergent, and their intersection is defined by the following relation: [14]

[14] See reference 5.

$$\left(\begin{array}{c}\text{Ionic con-}\\\text{centration}\\\text{of favorable}\\\text{substance}\end{array}\right)^{a} = \left(\frac{K^{b}\text{ sol. prod. of favorable substance}}{K^{c}\text{ sol. prod. of unfavorable substance}}\right)_{\substack{\text{Temp. of}\\\text{boiler water}}} \times \left(\begin{array}{c}\text{Ionic con-}\\\text{centration}\\\text{of unfavor-}\\\text{able substance}\end{array}\right)^{d}.$$

The intersection of the curves represents the condition in which both solid phases are in equilibrium with the boiler water; to insure the precipitation of favorable substance, the concentration indicated by the left hand term must be made greater than that of the right-hand term.

For the great majority of natural waters, calcium sulphate is the unfavorable substance which must not appear as solid phase in the boiler water. If the operating pressure of the boiler is not too great, the attainment of this end is accomplished economically by making calcium carbonate the favorable substance. Under these conditions the general formula may be written as follows:

$$\left(\begin{array}{c}CO_3\\\text{p.p.m. in}\\\text{boiler water}\end{array}\right) > 5/8\left(\frac{\text{K sol. prod. } CaCO_3}{\text{K sol. prod. } CaSO_4}\right)_{\substack{\text{Temp. of}\\\text{boiler water}}} \times \left(\begin{array}{c}SO_4\\\text{p.p.m. in}\\\text{boiler water}\end{array}\right).$$

If the pressure of operation is 150 lbs. gage (185° C.), the formula becomes:

$$CO_3 \text{ p.p.m.} > 0.0883\ SO_4 \text{ p.p.m.}$$

At the temperature of boiler waters, and the low partial pressure of carbon dioxide characteristic of the rapidly generating steam, the decomposition of carbonate radical with simultaneous development of hydroxyl radical and gaseous carbon dioxide is rapid. The hydroxyl concentration is necessary for prevention of magnesium silicate formation, as it minimizes the concentration of magnesium ion in the boiler water. The success of internal treatment when concentration of carbonate radical is maintained as demanded by the sulphate concentration, and the amount of sludge in the boiler water is controlled by a filter attached to the boiler, is attested by the condition of the steam drum shown in Fig. 3. More than 120,000,000 lbs. of steam have been generated in this boiler since this system of treatment was inaugurated.

Thin Scales, Sludges, and Steam Line Deposits

The characteristics of the thin scale, sludges, and steam line deposits developed with this type of treatment in a number of boilers are summarized in Table 6. As long as the essential excess carbonate concentration corresponding to full treatment was maintained in the boiler, the amount of sulphate and silicate in the scales was low, and they remained very thin. When such conditions were not maintained, however, both silicate and sulphate increased, as in No. 4 and 5, or sulphate alone as in No. 6, which is a nearly pure anhydrite scale. The growth of such scales is retarded by the partial treatment, but is certain. In the sludges and steam trap deposits, the per cent of magnesium silicate is markedly higher than in the scales, as indicated by Nos. 7–12 inclusive. The large proportion of magnesium silicate in the steam lines shows the preferential removal by the steam when it carries moisture of those substances in suspension which are of a finely divided or flocculent character.

Microscopic examination of all the samples has been impossible; but the relations between the chemical and the microscopical characteristics of those examined has been so definite that the additional chemical analyses can be interpreted satisfactorily.

Conditions Under Which Treatment with Soda Ash Fails

Because of the rapid decomposition of carbonate radical at operating pressures in the neighborhood of 200 lbs. gage and above, it is impossible to prevent the appearance of calcium sulphate as solid phase with soda ash unless the sulphate concentration is maintained very low. Thus in a 1950 h.p. Bigelow-Hornsby boiler, operating at 160 lbs. gage pressure, the feed water (100 per cent make-up of water containing sulphate hardness) entered tube elements F and E, in which little or no evaporation occurred; then passed to elements D and C, in the main boiler circulation, but behind the steam drum. The final elements in the main boiler circulation are B and A, which are in front of the steam drum and are supplied with water by its inflow from elements C and D. The heat flow was in the direction $A \rightarrow F$.

TABLE VI

THIN SCALES, SLUDGES, AND STEAM LINE DEPOSITS, WHEN WATER IS TREATED ON BASIS OF THE CARBONATE-SULPHATE RATIO IN THE BOILER WATER. (ANALYSES IN PER CENT)

No.	Treatment of Water	Type of Deposit	SiO_2	Al_2O_3 Fe_2O_3	CaO	MgO	SO_3	CO_2	Loss at 105° C.	Ignition Net Loss	Microscopical Analysis
1	Full, internal	Thin on tubes	2.2	3.4	49.9	3.0	2.2	38.3	0.1	1.3	Calcite
2	Full, internal	Thin on steam drum	4.6	12.9	37.6	6.2	1.3	34.9	0.1	3.1	Calcite; a very thin scale over a scale of iron rust, Small amount of brownish isotropic material (magnesium silicate) and a little coarse anhydrite.
3	Full, internal	Thin, loose, from water screen	5.5	4.2	44.9	6.9	0.5	34.2	0.1	3.5	Calcite; ferric oxide; brownish isotropic material, much of which serves to bind the calcite grains. Part of the scale is studded on both sides with crystals, showing that it had been loose for sometime before the scale was collected.
4	Partial, internal	Medium thick from tubes	13.5	3.7	29.6	7.3	8.1	20.1	0.6	7.6	
5*	Partial, internal	Medium thick from tubes	1.8	4.6	39.9	2.9	22.4	21.2	0.1	2.1	Abundant anhydrite; calcite; hydrated‡ magnesium silicate
6	Partial, internal	Thin, from tubes	1.6	0.6	39.1	4.6	46.0	4.6	0.3	3.0	
7	Full, internal	Sludge from filter attached to boiler	5.2	3.4	42.1	9.4	1.2	32.2	0.2	6.5	
8	Partial, internal	Sludge from boiler	0.2	1.6	43.0	10.2	1.9	40.3	0.2	3.9	Calcite; hydrated magnesium silicate‡
9	Partial, external with sodium phosphate	Sludge from filter attached to boiler	10.9	11.7	27.4	10.3	7.3	P_2O_5 18.5	0.7	11.3	Anhydrite; the remainder is fine and almost clay like†
10	Full, internal with soda ash	Steam trap deposit	5.4	7.2	37.6	10.6	1.2	28.6	0.5	10.2	Calcite; brucite; hydrous magnesium silicate‡
11	Full, external lime-soda ash filtered	Deposit from superheater headers	10.6	6.3	18.9	26.4	6.6	14.4	1.1	14.6	Calcite; brucite; hydrous magnesium silicate‡
12	do	Steam trap deposit	12.5	7.8	19.2	28.0	2.0	14.7	2.0	15.3	Calcite; brucite; hydrous magnesium silicate§

* This scale contained also: Cl, 0.1 per cent; Na, 3.2 per cent. † The analysis indicates that the finely divided material must consist mainly of calcium phosphate, and magnesium silicate. ‡ Microscopic examination by R. DeChicchis, Carnegie Inst. Tech. Research Fellow. § This microscopic analysis was made by A. H. Emery, Asst. Geologist, Bureau of Mines.

TABLE VII*

SCALES AND SLUDGE FROM BIGELOW-HORNSBY BOILER

Treatment of water: Lime-soda ash with filtration.

Excess carbonate concentration was based on the carbonate-sulphate ratio in the boiler water, but carbonate decomposition rendered its maintenance impossible in *A* element. (Analyses in per cent.)

No.	Type of Deposit	SiO_2	Al_2O_3 Fe_2O_3	CaO	MgO	SO_3	CO_2	Loss at 105°	Net Ignition Loss
1	Thin scale on tubes of *C* element	2.5	3.2	50.0	3.7	1.8	37.6	0.2	1.5
2	Sludge in bottom headers of *B* element	11.7	8.1	25.8	20.9	6.0	16.7	0.7	11.6
3	Medium thick scale on tubes of *A* element	0.8	0.5	40.4	1.5	53.3	0.6	0.3	0.9

* Analyses by J. A. Robb, Hagan Corporation.

In Table VII, No. 1 gives the composition of thin scale found in the tubes of *C* element; No. 2, that of sludge found in the bottom headers of *B* element, where it was not disturbed by circulation or blow-down; and No. 3, that of well developed medium thick scale found in the tubes of *A* element.

The scale of *C* element is low in sulphate and magnesium silicate, and is thin. It is typical of the results obtained when the carbonate concentration has been sufficient to preclude calcium sulphate as solid phase. The composition of the sludge corresponds very closely to that of the deposit from superheater headers, No. 11, Table VI, or from the steam trap, No. 12, Table VI, showing as the main constituents calcite, brucite, and magnesium silicate, with smaller per cent of anhydrite and ferric oxide. The scale in element *A* is almost pure anhydrite. Such a scale results from sulphate equilibrium obtaining persistently; and the absence of magnesium silicate bespeaks high hydroxyl concentration which maintained the magnesium concentration very low at all times. Evidently, circulation in the *A* and *B* element was largely localized, and the maintenance of excess carbonate concentration dependent wholly upon the inflow of water from *C* element to replace that evaporated. Wherefore, a high proportion of the carbonate decomposed, and this element of the boiler was on sulphate equilibrium.

The remedy for a condition such as this is to substitute for carbonate a radical such as phosphate which does not decompose at

boiler-water temperatures. The use of this radical in boilers operating at 320 lbs. gage, and in concentrations based on the sulphate content of the boiler-water, has proved very satisfactory.

Deposits from Corrosion and Other Causes

No. 1, Table VIII, is of interest because it represents the product obtained from evaporating a water from which No. 11, Table II, was deposited, as adherent scale. Sodium sulphate and carbonate, and magnesium silicate are apparently the main components, though their certain identification was not obtained.

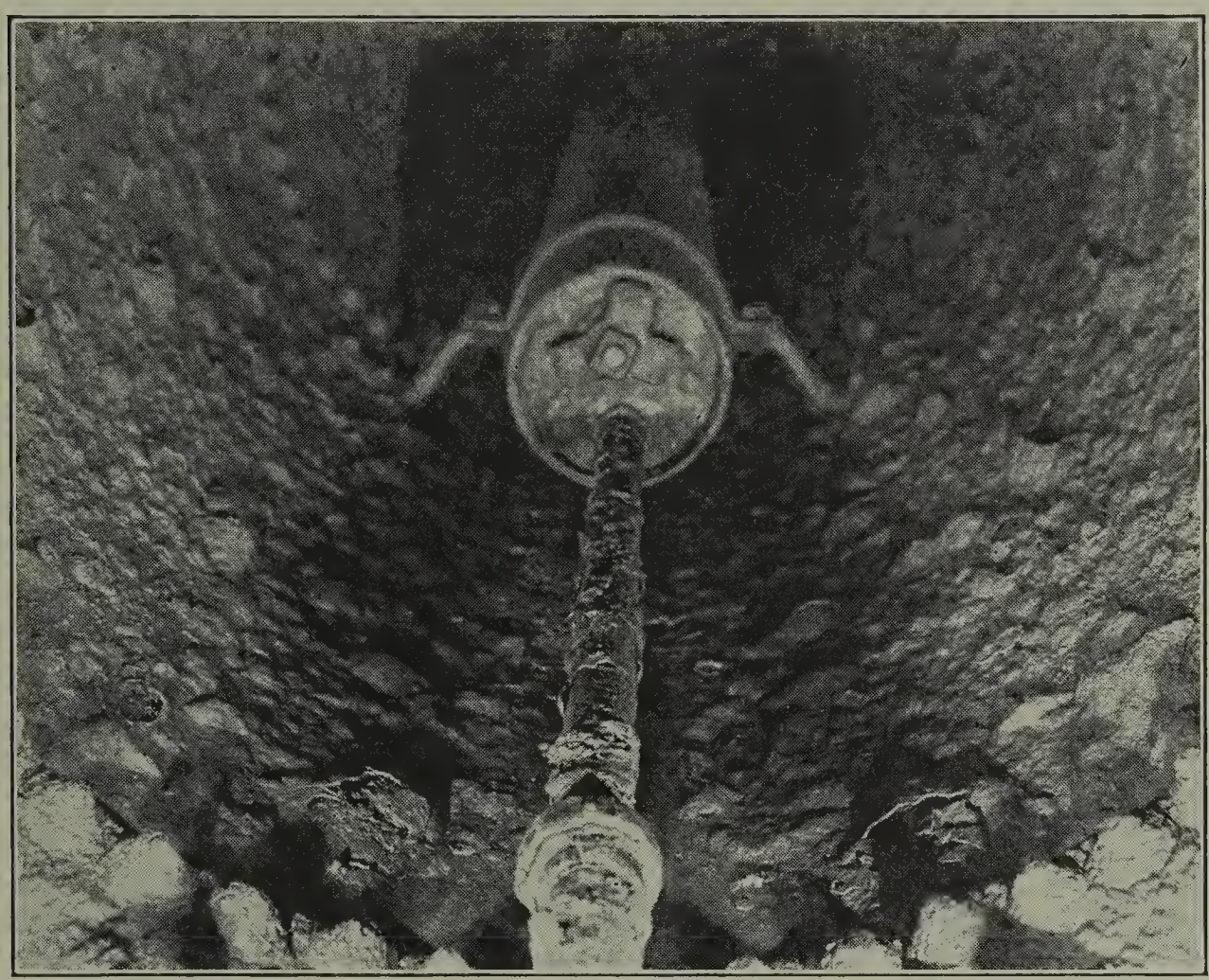


Fig. 2. Boiler Scale and Corrosion on Steam Drum after the Evaporation of 58,334,000 Lbs. of Water

The presence of ferrous and ferric sulphate, as found in No. 2 of this table, seems to indicate an acid condition—a thing which is undesirable to say the least.

The large amount of ferric oxide in the corrosion deposit (No. 3) found in a superheater, is indicative of action by air, as it had access to the surfaces during a few periods when the boiler was not in operation. The ferric oxide of No. 4 may be ascribed to the same

TABLE VIII*

CORROSION AND OTHER DEPOSITS. (ANALYSES IN PER CENT)

No.	Source	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	Na_2O	SO_3	CO_2	Cl	Loss at 105°	Net Ignition Loss	Microscopic Analysis
1	Valve stem light colored deposit from leakage and evaporation	10.9	(	0.9	)	1.7	15.9	42.8	13.4	11.6	—	2.8	—	This is largely a definitely crystalline substance for which no recorded optical properties were found. It is probably a sulphate-carbonate of sodium, which may contain hydroxide, also, as might be expected from the temperature of formation. The salt is very soluble in water
2	Steam line light colored deposit from corrosion probably	0.4	0.9	19.8	24.0	0.6	0.3	3.3	40.2	—	1.4	1.2	9.2	This is largely a homogeneous crystalline scale of what is probably a basic ferrous-ferric sulphate which is not known, as a mineral
3	Superheater. Hard, thick red deposit from corrosion	4.2	3.2	82.7	6.1	1.2	2.1	0.6	0.2	0.2	—	0.1	0.4	Largely ferric oxide

TABLE VIII*—*Continued*

No.	Source	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	Na_2O	SO_3	CO_2	Cl	Loss at 105°	Net Ignition Loss	Microscopic Analysis
4	Headers. Around Staybolt. Red scale and corrosion	6.4	(	14.8	)	30.0	8.5	—	30.4	6.8	—	0.1	5.6	
5†	Steam drum. Non-magnetic, finely divided loose light colored material under blisters of hard scale	4.6	2.2	4.5	1.2	30.7	7.8	—	42.4	0.1	—	0.3	6.4	
6‡	Steam drum. Magnetic hard black deposit. Thick under blisters, but extending almost continuously under the sulphate scale. Corrosion	2.0	0.7	38.8	16.0	13.8	3.0	—	19.6	0.2	—	0.2	4.4	Intimate mixtures of anhydrite, and a black substance which is undoubtedly magnetite, although it cannot be identified microscopically, except that its strong magnetic properties cause it to string together in the mounting liquid. Magnetic separation of such fine-grained materials is practically im possible

* Analyses by Grace Thomas, Hagan Corporation.

† The original sample contained 12 per cent of magnetic material similar to No. 6 of this table; this was separated before the analysis was made.

‡ The original sample contained 0.5 per cent of non-magnetic material which was separated before the analysis was made.

source of oxygen, as the feed water entering the boiler passed through the header from which the scale was taken before entering the tubes.

Nos. 5 and 6 are the deposits from under the blisters shown in Fig. 2. Under each blister was found loose light colored finely divided material, and beneath, a hard, black scale, thickest under the blister, but extending almost without interruption over the entire surface. Under the thickest portion of the black scale, invariably a pit was found.

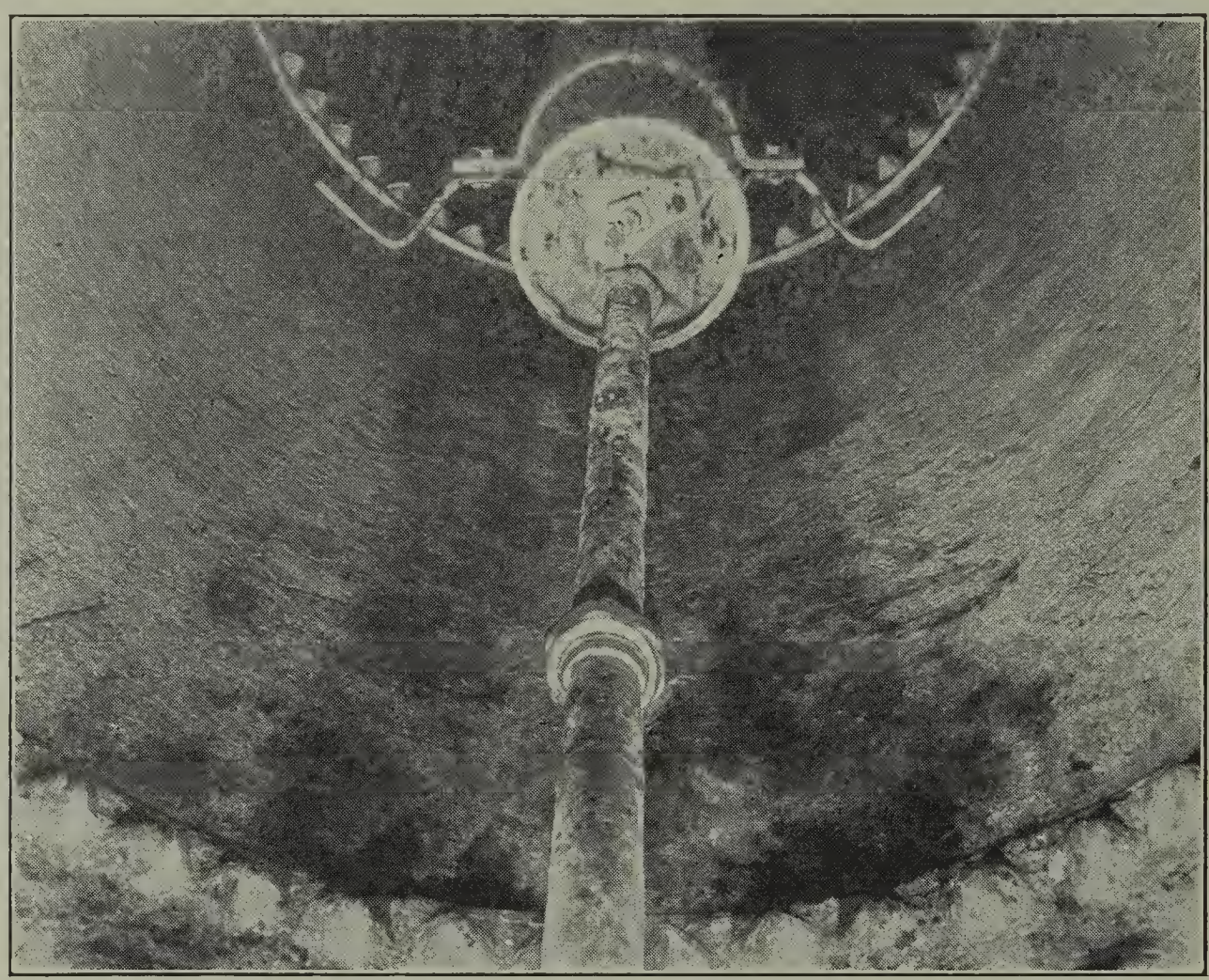


Fig. 3. Typical Condition of Steam Drum Surface when the Appropriate Carbonate Sulphate Ratios have been Maintained

As shown by the analysis (No. 5) the loose material, freed from any fine particles of the black substance by magnetic separation, was quite analogous to the customary anhydrite scales. The black material, on the other hand, finely pulverized, and freed as far as possible of any non-magnetic substances, still contained considerable anhydrite. The ferric and ferrous oxides are very closely in the proportions required for Fe_3O_4; and anhydrite and magnetite are present very closely in the molecular proportion of 1 : 1. The

microscope shows that these two components are present as an intimate mixture; and only further investigation of a number of samples can determine whether occurrence in molecular proportions was a coincidence, or the rule for this type of deposit.

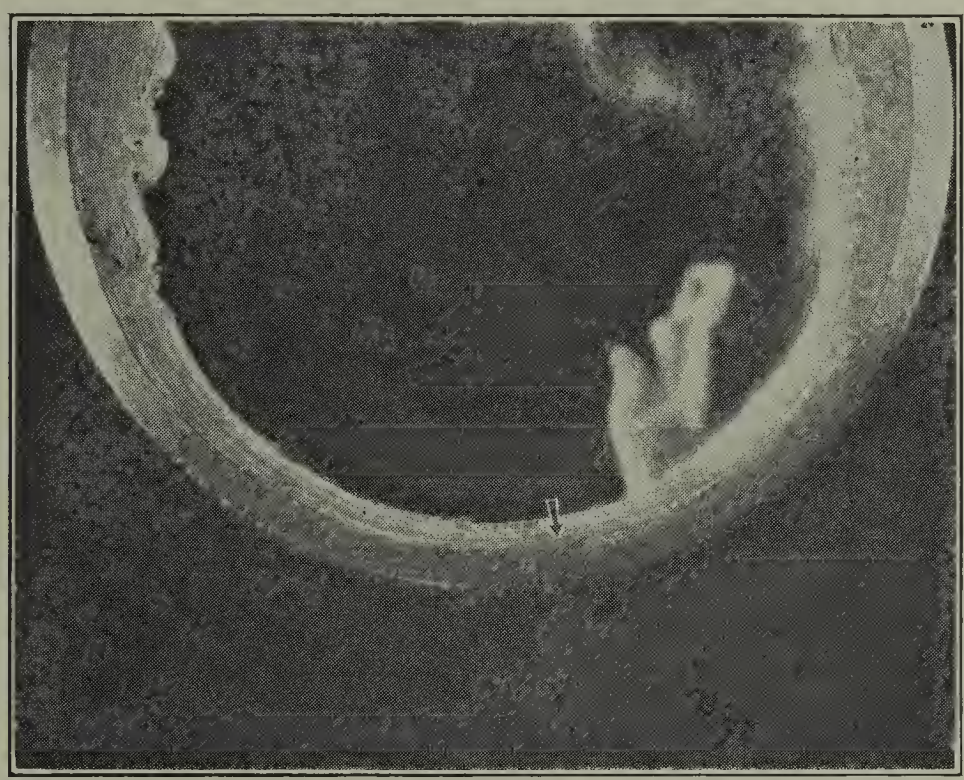


FIG. 4. Pit Formation under Sulphate Scale. The arrow indicates the point at which this formation is occurring

The evaporating surfaces of a boiler are usually covered with a film of black—probably magnetic—oxide, whether scale is present or not, and the amount of hydrogen in the steam seems closely related to the hydroxyl content in the boiler water. This points to direct reaction of metal and water at the evaporating surfaces; but with 100–200 p.p.m. of hydroxyl in the boiler water, pit formation is apparently negligible.

A different condition exists, however, when the metal surface is covered by dense anhydrite scale. Thus the arrow in Fig. 4 indicates a point at which pit formation is taking place, and Fig. 5 shows a tube failure ascribable to this cause. In both cases the cross section showed a black layer between the metal and the dense anhydrite. When examined with a strong lens a few days after being sectioned, there appeared between the metal and the black layer a thin white film which proved to be $FeSO_4.4H_2O$. This hydrate could not have been stable under the operating conditions in the boiler and must have formed subsequently from material in the black layer. Microscopical examination of this layer showed

one, and in some places two, transparent constituents besides anhydrite, in a very finely granular mixture with magnetite. These have not been identified. As the boiler water in the plant from which the sample was obtained has never been found to be acid in three years of observation, the most feasible explanation of the ferrous sulphate formation seems to be electrolytic action in connection with the pit formation.

Fig. 5. Corrosion under Sulphate Scale Has Resulted in a Blown Out Tube

Conclusion

Study of the solid phases developed when natural waters with and without treatment were evaporated at boiler pressures, has led to a conception of the mechanism of scale formation. Deposition occurs *in situ* except for pieces of scale which may be torn loose and then incorporated in the growing scale by further crystal formation on the surfaces of contact. A criterion which determines whether precipitation occurs as adherent scale or independent particles is the slope of the solubility curve of the solid phase precipitating; if dS/dT is negative, deposition occurs largely as adherent scale, and if positive, largely as sludge. Satisfactory boiler-water treatment must result in non-adherent particles as the solid phase in boiler-waters; and since the solubility curves of scale-forming and sludge-forming substances are divergent, the concentration of treating chemical necessary in the boiler water is a function of the operating pressure of the boiler, and the concentration of unfavorable ion. The substances mainly responsible for the growth of adherent scale have been shown to be calcium sulphate and magnesium silicate. Maintenance in the boiler water of conditions

which inhibit their deposition on the evaporating surfaces in appreciable quantity, not only prevents the growth of adherent scale, but minimizes corrosive action on the surfaces.

ACKNOWLEDGMENTS: The authors take pleasure in acknowledging the support and assistance throughout the investigation of A. C. Fieldner, superintendent and supervising chemist, Pittsburgh Experiment Station, and J. M. Hopwood, president of Hagan Corporation.

DISCUSSION

THE CHAIRMAN: Are there any questions, gentlemen, or any discussion of this paper?

MR. BARR: Mr. Chairman: I would like to ask Mr. Smith if the chloride concentration there is taken into consideration and to what extent?

MR. SMITH: We have considered the chlorine concentration as contributing to the total solids, and have used it as a means of determining the ratio of concentration reached between the boiler water and feed water.

MR. BARR: Would you consider then that the concentration of the chloride ions does not have any effect on the adjustment of its carbonate balance?

MR. SMITH: We believe it does, but only to a slight extent. We know the solubility of calcium sulphate increases slightly in the presence of chlorides. The effect of chloride at first sight would seem to be to decrease the numerical value of the ratio of the solubility product of calcium carbonate. However, calcium carbonate and calcium sulphate being salts of similar ionic type, the ionization of which depend on total ionic concentrations of which the chloride ion concentration is only a part, their apparent solubilities should be altered similarly, and the ratio of their solubility products should be largely independent of other ionic concentration.

MR. BARR: It seems to me, Mr. Chairman, that there has been some very interesting and important data brought out in this paper concerning the character of scale formations and the mechanism of scale formation. In the application of this principle, however, it seems to me it is of more value in the adjustment of the chemical equilibrium in the treatment of the boiler water before entering the boiler than in the internal treatment. It is almost an axiom among those of us who have tried to treat it with scientific accuracy that it is preferable to use clean softened water to dirty water. Many

of us find that we have to use boiler waters having high sulphate concentration and if you have to use a hot process treatment, so that the scale forming material is reduced from .0724 to seventeen millionths of calcium solids, the concentration in the boiler can be carried higher without further danger of formations, thereby reducing the fuel losses by blow-offs and the injury to turbines that are caused thereby, so that we can get more satisfactory results. Take, for example, in the larger installations of water-tube boilers, a 256 horsepower Stirling unit would probably evaporate in the neighborhood of ten millions pounds of water per month. Therefore, if your increased solids in that treated water do not exceed 20 parts per million, at the end of thirty days we only have about 200 pounds of scale-forming material. This without taking into account the condensation from the boilers and the amount of soft, non-adherent sludge that would be formed, but taken care of in the blow-off. It, therefore, seems to me that applying this principle to adjusting the mechanical equilibrium of the water before it goes into the boiler makes it of great value, and that it would be desirable to do that.

Mr. Smith: We have applied these principles to treating in plants of both types; where we desired to treat inside the boiler, and where existing installations forced us to treat outside the boiler. In the latter case the correct adjustment of treatment, by means of the principles under discussion, insures the precipitation of the residual hardness as non-adherent calcium carbonate, which may be removed as sludge rather than adherent calcium sulphate. The boiler waters resulting from the two methods of treatment are approximately the same. The analyses of the filtered solutions would be identical and the nature of the solid phases the same.

We also have used a pre-treated water, in 1,950 horsepower boilers—I intended to come to that this morning—where we treated approximately 10,000,000 pounds of water a day and got the hardness down to practically the lowest figure we have been able to obtain, say about 25 parts per million. Even under these conditions, we were putting into these boilers, approximately 250 pounds per day of material which had to precipitate. We felt it necessary to control this, so that it would come down as suspended material and be removed by the blow-down which was necessary to take care of the dissolved solids. We all believe that suspended solids should be kept down in a boiler as far as possible.

MR. BARR: I would like to ask Mr. Smith: If you get that chemical equilibrium, will you not have that same control?

MR. SMITH: We would have the same control but it would not be as easily accomplished, as we see it, by actual plant apparatus. In control of boiler water conditions by boiler water analysis, we deal with much more concentrated solutions and errors of titration are of little significance. It is necessary to have very careful titrations to control the condition of feed waters.

MR. BARR: Do you not find that you can keep equilibrium correct if you can teach the men to handle the titrations and also teach them to control the water from the treating plant?

MR. SMITH: Also, it is impossible to reduce the amount of scale-forming material much below 25 parts per million by means of lime-soda pre-treatment, and the type of precipitate formed by this material depends upon the conditions in the boiler. To adjust these by feed water titration involves a definite knowledge of the rate of carbonate decomposition under boiler conditions which is not available at the present time, but which is known to depend so largely on operating conditions that it is doubtful whether even with much more definite information, the carbonate concentration could be satisfactorily predicted.

We might be able to do it but it has been our experience that we have never failed to teach the men to determine boiler water conditions correctly, but it has often been found difficult to teach them to treat the feed water properly.

PRESIDENT REESE: Is there any further discussion? If not, we will have a paper by Dr. James G. Vail, entitled, "Some Properties of Doucil, a New Base Exchanging Silicate."

SOME PROPERTIES OF DOUCIL, A NEW BASE EXCHANGING SILICATE

By JAMES G. VAIL,

Vice-President, American Doucil Company

Read and Discussed at the Pittsburgh Meeting, December 4, 1924

Natural zeolites soften water and are in turn regenerated by salt brines by reactions which occur at or very near the surface of the mineral particles. A part of the sodium content of the interior of the grains is therefore not available for replacement by equivalent quantities of calcium or magnesium. It is locked up, if not entirely out of contact with water, at least away from any appreciable circulation. If this conception be true, it follows that by crushing to smaller size and thus increasing the surface exposed by a unit weight of zeolite, the efficiency of the reaction will be increased, and this is borne out in actual experience. Water softeners for industrial purposes, however, impose a limitation on the size of grains that may be employed. If the mineral is too fine, it offers too great a resistance to the flow of water and is too easily washed out of the softener. Under conditions appropriate for practical use only about one fifth of the sodium oxide content of glauconite or greensand is available for replacement with lime and magnesia from hard waters. The rest is enclosed within the substance of the mineral and the reasons for its lack of activity appear to be principally mechanical. The low efficiency of the reactions is easily overlooked because even very hard waters are dilute solutions and consequently large volumes may be treated per unit of mineral. Thus, a cubic foot of greensand, which weighs ninety pounds and is capable of binding the equivalent of 2700 grains of calcium carbonate, will soften 270 gallons of ten grain water between regenerations and yet the calcium oxide involved is less than a quarter of one per cent of the weight of the greensand.

Greensand has the advantage of reacting quickly with both hard water and salt solutions. The surface sodium oxide can be exchanged for lime or magnesia in solution on very brief exposure and when the grains are immersed in a solution of common salt, the lime

and magnesia are exchanged back again making a sodium zeolite on exposures of less than five minutes.

The attempt to make artificial base exchanging silicates of higher capacities by producing porous structures, has, even in those cases where a substance intrinsically as reactive as Glauconite was produced, been accompanied with a lag corresponding to the time necessary for water to penetrate the porous structure. In an industrial softener this means that as the mineral nears the point of exhaustion it begins to deliver water incompletely softened instead of showing a sharp end point as most natural zeolites do.

Some of the artificial products devised previous to the advent of the one about to be described are intrinsically less reactive, requiring to be soaked in salt solutions over night for the purpose of regeneration, but others, notably those precipitated from dilute sodium silicate solutions with soluble aluminum compounds combine a relatively high capacity with quick regenerating properties. One of the best of these weighs about 32 pounds per cubic foot and will take up approximately 5,000 grains calcium carbonate equivalent, but even this represents but one and a quarter per cent of calcium oxide bound by the base exchange material. With such a product, 500 gallons of ten grain water can be softened per cubic foot at each regeneration.

Doucil is distinguished from all other base exchanging silicates by its structure. It is a gel, which is to say that it is a fine cellular body having pores of submicroscopic dimensions, evidently arranged with considerable uniformity and capable of strong capillary action. It is prepared by the complete gelation of a solution made from sodium silicate and sodium aluminate under such conditions of control that its properties are definite and reproducible. The gel structure exposes to the action of water and salt solutions a surface which is greatly in excess of that presented by a system of coarser or less uniform pores. The effect is seen in a substance of increased exchange capacity. Another product of like composition but different structure may be useless for exchange purposes. A cubic foot of Doucil contains 25 pounds of anhydrous silicate capable, under practical working conditions, of absorbing 12,500 grains of calcium carbonate equivalent, or 4 per cent by weight of calcium oxide. This is to say that a cubic foot of Doucil will soften 1,250 gallons of 10 grain water in comparison with 270 gallons of the same water for a like volume of greensand. Twelve thousand grains per

cubic foot is believed to be higher than any record of sustained performance of other base exchanging materials. It is a conservative figure for Doucil, as several tests of domestic softener units are in hand which show substantially higher exchange rates. It may also be noted that the comparison on the volume basis is the least striking though the most significant for practical use.

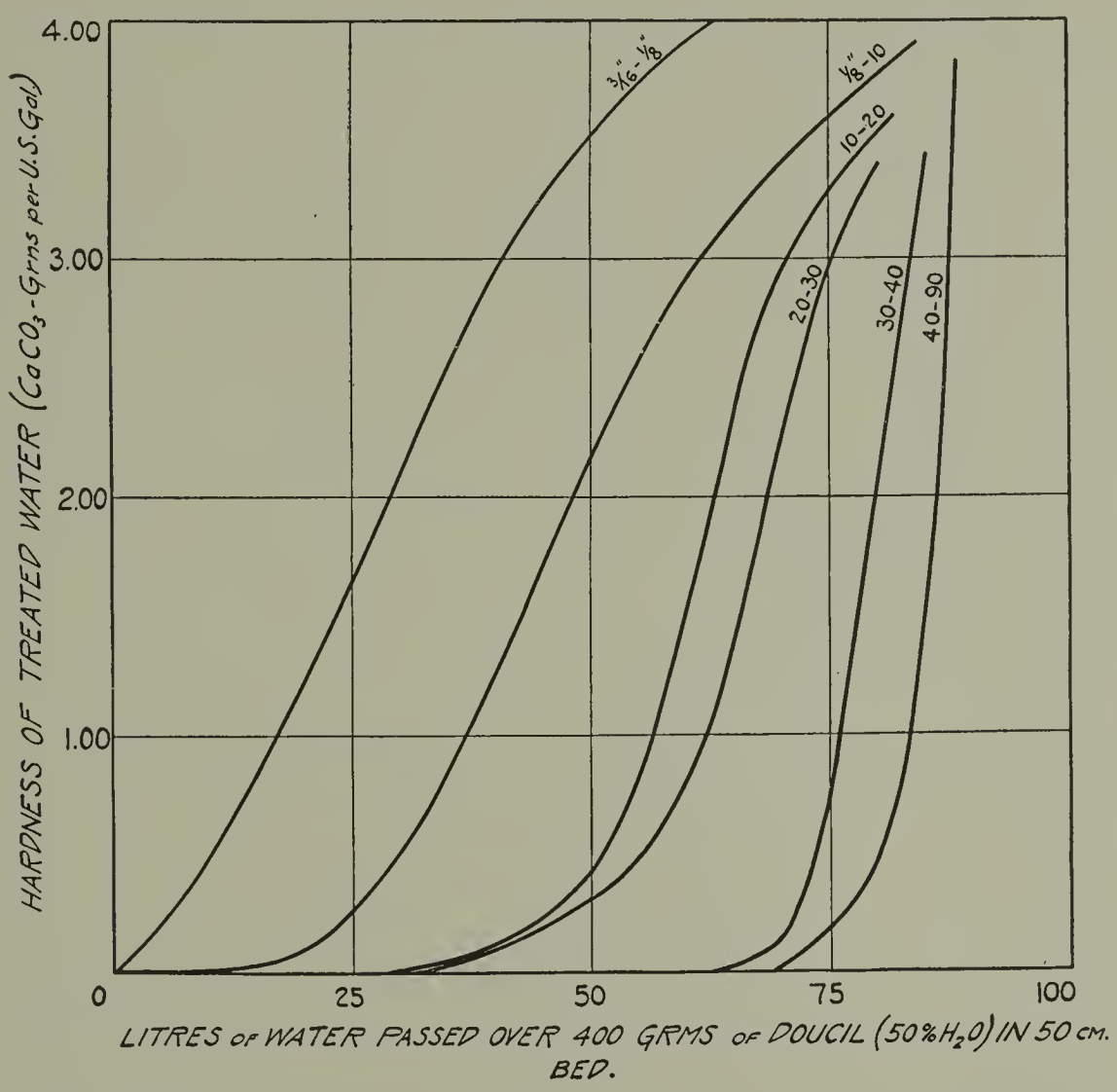


FIG. 1. Relation of Size of Grain to Proportion of "Zero Hardness" Water Produced

Those familiar with the art of softening water will be quick to realize that such a result can be obtained only with apparatus designed and operated in a manner compatible with the characteristics of the gel, but the figures given are based on experience in actual service on a considerable variety of waters with apparatus of industrial size in continuous service. Most of the laboratory work has been done with a water of approximately 17 grains hardness containing calcium and magnesium bicarbonates in the proportion of four to three.

The molecular composition of Doucil approximates $Na_2O.Al_2O_3.5SiO_2$. Contact with solutions of calcium and magnesium salts in excess will cause the exchange of almost all of the sodium content, but the reaction is not sufficiently rapid to permit this to be attained when a single cell is required to deliver water softened below one grain calcium carbonate equivalent per gallon. As with the greensand, the higher efficiencies are secured with the smaller grain sizes. Fig. 1 shows the extent of softening accomplished by

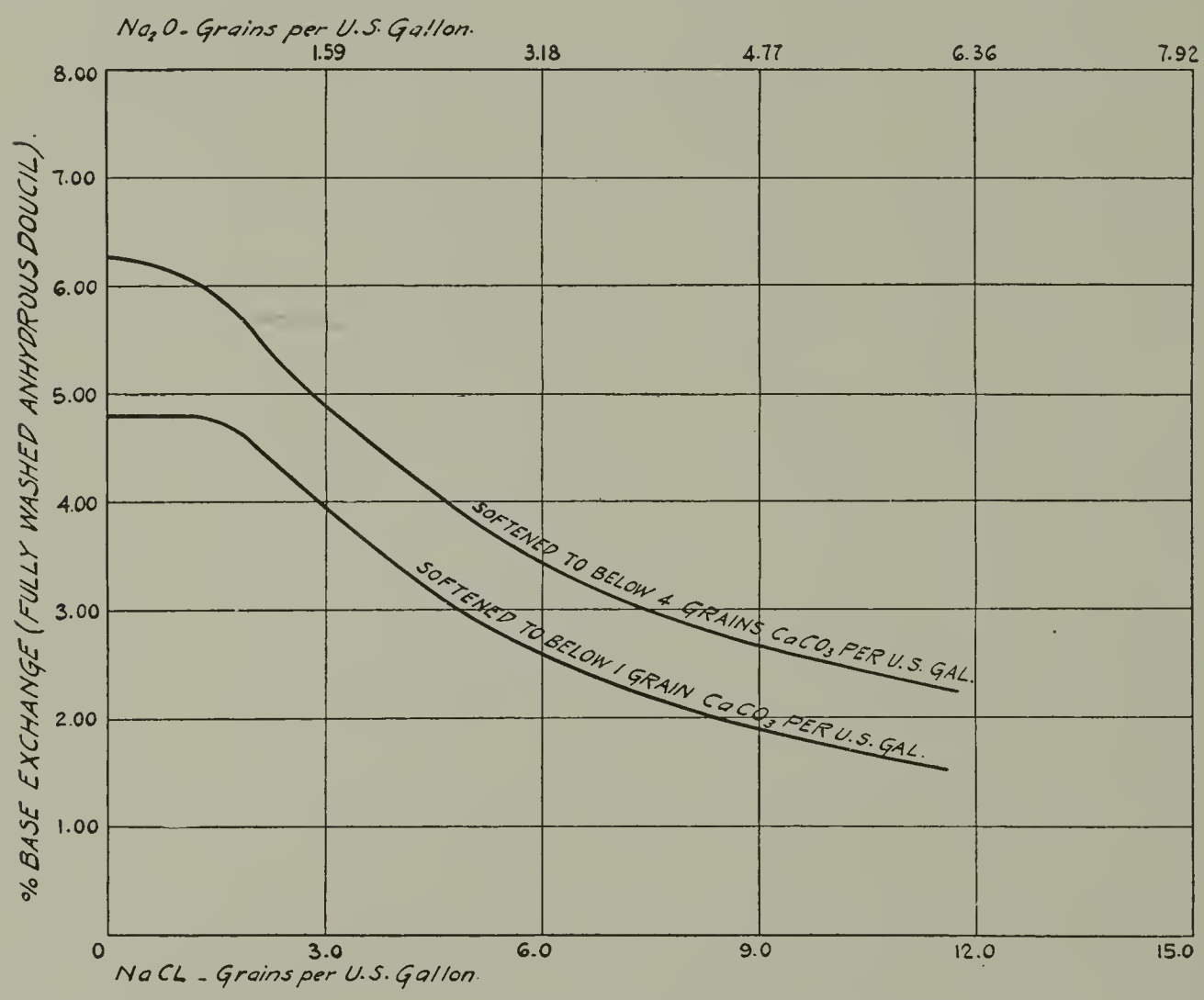


FIG. 2. Effect of Sodium Chloride in Hard Water

different sized Doucil particles in tube tests yielding water below a hardness of one grain. If instead of, so-called, zero water, a greater calcium carbonate content is permissible in the softened water, the Doucil will show a higher yield. This is set forth in Fig. 2. In other words, the end point is not perfectly sharp and increased volumes of water may be handled in a single cell if the tolerance of hardness in the treated water be increased. Fig. 2 also shows the effect of sodium chloride in the raw water. It is obvious that with a

substance which can be regenerated with a salt solution, we have to deal with a reaction which may proceed in either direction. In the presence of hard water, calcium Doucil is being formed and sodium salts corresponding to the radicals of the calcium or magnesium salts in the hard water are passing into solution. The rate and extent to which these reactions proceed is a question of equilibrium. A pure solution of sodium chloride will react very quickly with completely exhausted Doucil and conversely completely regenerated Doucil reacts rapidly with hard water. It will readily be seen that if the hard water contains sodium chloride, the tendency of the Doucil to bind lime and magnesia is suppressed in greater or less degree depending on the concentration of salt. Doucil is not capable of removing lime and magnesia from sea water and as shown in Fig. 2, its capacity is reduced by any sodium chloride or other soluble sodium compounds which may be present in the water. It has, however, been found practicable to treat waters containing as much as 33 grains Na_2O per U. S. gallon on a plant scale operation in which a 3 per cent exchange on the anhydrous basis is being achieved. The installation on which this record was made is located adjacent to natural salt brines, so that it was both economical and convenient to use a large excess of salt for regeneration. The water was softened from 11 grains equivalent calcium carbonate to less than one grain. Of the 33 grains Na_2O, approximately one half of the sodium was present as carbonate and sulphate, the remainder as chloride.

Some waters are not suited to treatment with Doucil. Those containing hydrogen sulphide tend to deposit sulphur upon the surface of Doucil grains, clogging the capillary system thus putting it out of action. Similar effects are produced if the water contains oil or any suspended matter which is not easily washed from the surface of the grains. Every precaution should be used to keep these active surfaces clean. Waters of low alkalinity which have presented great difficulties to other synthetic base exchange materials have been successfully treated with Doucil. In fact, solutions of calcium sulphate only have shown normal exchange rates on a laboratory scale of experiment.

Doucil is a colorless, translucent substance. Its grains are angular in contour and remind one of pieces of opalescent glass. Its hardness is sufficient to enable it to remain unchanged over long periods in contact with water and to resist the mild abrasion which

occurs as the water softening bed is traversed by the water to be softened or lifted and rearranged in the course of back washing. The fine porous structure of Doucil makes it necessary to keep it moist. If it were completely dehydrated and then dropped into water the rush of liquid into the capillary system from all sides would compress air in the interior and cause the grains to split. Accordingly it is brought upon the market with the pores full of water, for which about 50 per cent by weight is required. If this water is allowed to freeze, some of the larger grains will split, but practically no pieces smaller than 30 mesh are thus produced, so that no serious results are encountered especially in view of the fact that there are other reasons than possible damage to the base exchange material for protecting water softeners against freezing. The voids between the water filled grains are close to 48 per cent.

Doucil is not, strictly speaking a zeolite, as both natural and artificial zeolites contain more than 30 per cent alumina and Doucil contains less than 25 per cent. Another distinction lies in the behavior of zeolites, which tend to gelatinize and disintegrate in contact with dilute solutions of mineral acid. Under such treatment, Doucil does not change in physical appearance although Al_2O_3 and Na_2O are dissolved out and the exchange capacity lowered. No acid treatment is, therefore, available to cleanse Doucil which may have become contaminated in service.

Perhaps the question most frequently asked concerning a synthetic base exchange silicate is, how does it stand up in service. A great many products have been made which showed high capacities when first put into water and declined later as the number of regenerations increased, and the risk of such behavior seems to be greater with more porous and more active materials. Such disintegration is especially troublesome with colored materials which not only break down, but discolor the water in the process. Doucil is still comparatively new. The oldest industrial units are a little more than three years old and the maximum number of regenerations less than a thousand, but this time has not sufficed to indicate any disintegration of the grains or reduction of exchange capacity sufficient to be of practical concern. In this connection it might not be amiss to remark that the process by which such a refractory mineral as agate was formed appears to have been the action of water upon siliceous gels, the definite structure of which seems to impart a very durable character.

Since the softening and regenerating actions are not instantaneous, the method of softening with Doucil may be varied to give a desired result. If the maximum quantity of so-called zero water is of prime importance, it will be necessary to use a larger quantity of salt for regeneration than would be chosen in a plant where salt economy is considered first, whereas, if the maximum total of absorption of calcium and magnesium were paramount, a series of cells might be used permitting the complete exhaustion of one bed before regenerating. The greatest salt economy can be obtained by utilizing about 60 per cent of the exchange capacity and the maximum softening capacity can be secured with about 25 per cent utilization of the salt. The softening and regenerating processes are not simple cases of equilibrium. In addition to the chemical changes which would take place if complete contact could be secured at once between brine or hard water and Doucil, it is necessary to take into account the time required for those portions of the system of cells which are away from immediate contact with the solutions, to come into action. For this reason, we find that a bed of Doucil which is operated intermittently or with periods of rest will show a higher capacity than one in which the water is run continuously until it ceases to be completely softened and conversely some additional capacity can be secured by a longer contact with brine than is most suitable for ordinary operation. The first fractions of regenerating brine are almost quantitatively converted to calcium and magnesium chlorides. The first quarter of the regenerating solution removes about 50 per cent of the lime and magnesia and the first half from 80 to 85 per cent. This makes it convenient to use a salt saving scheme in which the first half of the regenerating brine is rejected and the second half saved for the first half of the next regeneration. The total consumption of salt is thus divided by two. The most efficient regeneration of Doucil is accomplished with a 5 per cent solution of salt. If salt is applied at double this concentration, about 10 per cent more will be needed to accomplish the same result.

It is customary to express the salt required for regenerating as pounds per thousand grains of calcium carbonate equivalent removed. The best greensands require about .5 pounds or 1.35 pounds of salt per cubic foot of mineral. On the same basis Doucil will require 6.25 pounds per cubic foot without salt saving and 3.1 with the use of this scheme. Experience has shown that this is

ample and some units are giving good service at substantially lower rates of salt consumption.

Doucil belongs to the class of quick regenerating base exchangers. Brief contact of the brine with grains of standard size is sufficient. The entire regenerating operation can be accomplished in thirty minutes with Doucil graded between screens of 8 and 30 meshes to the inch, having openings of .078 inch square and .0203 inch square

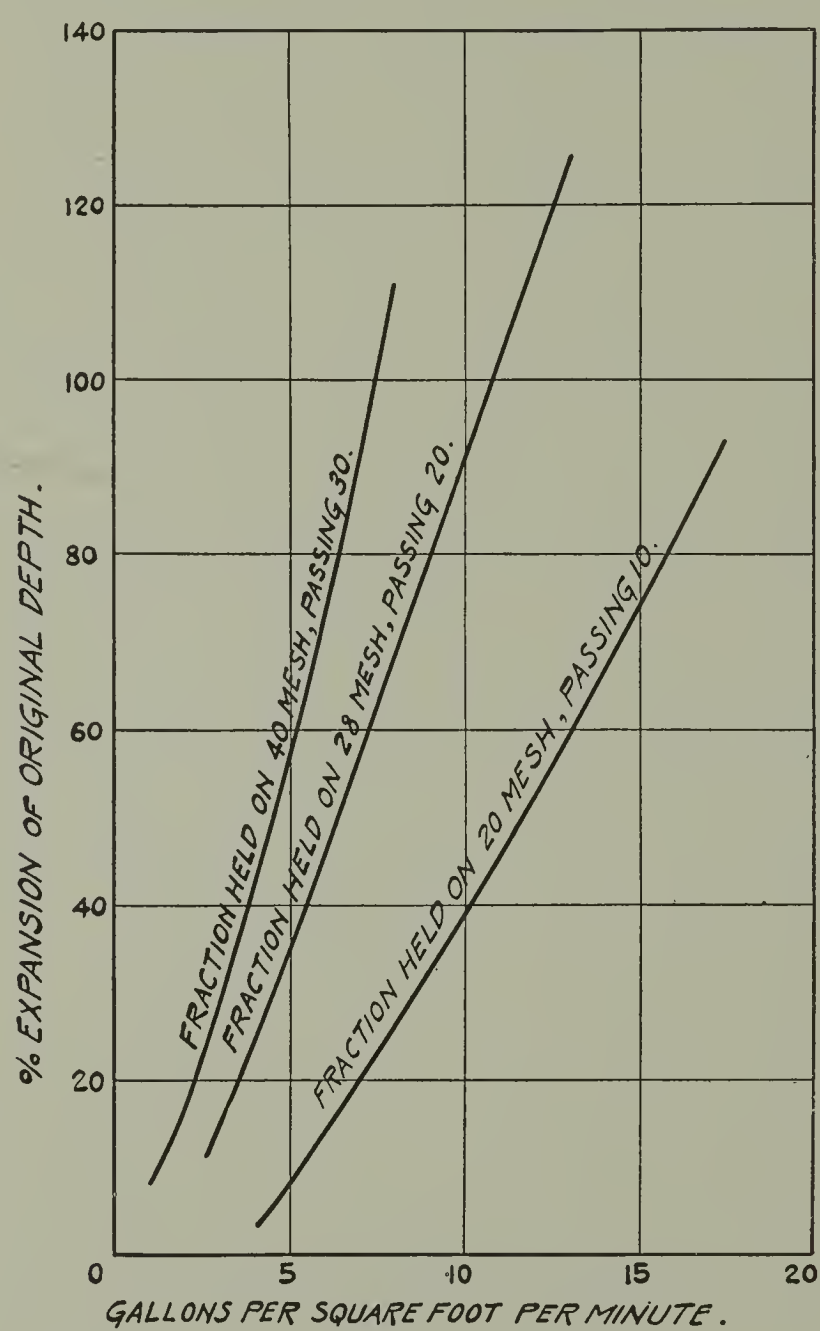


FIG. 3. Relation Between % Expansion and Back-wash Rate for Three Sizes of Doucil.

respectively. Incomplete regeneration does not permanently impair the exchange capacity of Doucil. This can be restored by soaking in brine using an amount of salt somewhat in excess of that normally required. Other reagents which are sometimes used with

other base exchange materials, should never be used with Doucil under ordinary conditions, although it has been found possible to remove mud which has soiled the surface of Doucil grains by deflocculation with a one per cent solution of sodium silicate having a ratio $Na_2O : 3.25\ SiO_2$.

The design of water softeners for using Doucil is not limited to any one type. Both down and up flow and various plans of regeneration are successfully used. The most important point to be borne in mind is the necessity of keeping the surface in an active condition. Down flow apparatus should be provided with back washing facilities sufficient to lift the bed and cause the rearrangement of the particles, thus avoiding any difficulties which might arise from the formation of channels through which hard water can flow before the last portions of the Doucil have taken up their quota of hardness. Back washing is also necessary to rid the bed of any suspended matter which may have filtered out of the water or separated from it by chemical reaction. Water which carries iron in solution, will stain the grains without, however, destroying their exchange capacity. Some of the iron will be removed in the regenerating brine. These same waters usually cause a deposit of flocculent ferric hydroxide, most of which can be removed by proper back washing. If a substance, such as ferric hydroxide, accumulates at the top of a down flow softener, it may practically seal up the flow of water and the pressure thus applied to the top of the bed may compress it reducing the depth of bed as much as 25 per cent without, however, doing injury to its capacity or ability to treat the water after back washing. As Doucil is lighter than other base exchanging silicates, it is possible to provide adequate back washing with a smaller flow of water than is needed for a heavy natural zeolite. The advantage of this for domestic softeners where the water flow is limited is considerable. As back washing is accompanied with an expansion of the bed, it is important to design the rate of flow and the head room above the Doucil bed in such a way that the grains are not washed out of the system. Assuming an even distribution of water, Figs. 3 and 4 show the effect of back wash at six gallons per square foot per minute on various grain sizes and the effect of various back wash rates on the standard 30 mesh grade. In both cases, this is expressed as increase of depth of bed.

Deep beds are in general more efficient than shallow ones because they not only permit all the water to make contact with the gel,

but they permit the complete exhaustion of the lower portions of the bed before hard water begins to flow through. Such considerations as rates of softening and periods of rest will determine what depth is best for a particular case, but in general beds less than 30 inches in depth are not to be recommended and beds up to 6 feet in depth are

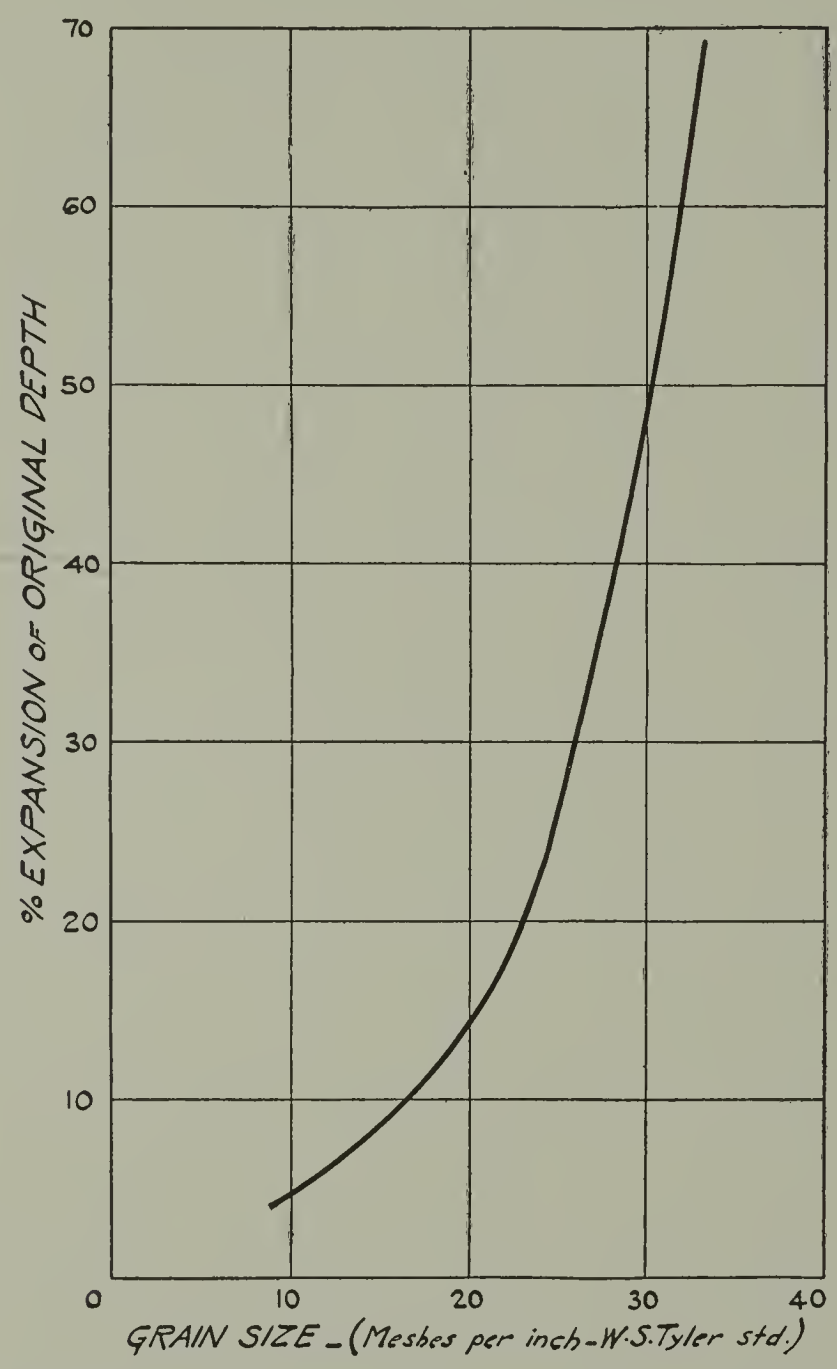


FIG. 4. Relation Between % Expansion and Grain Size When Backwashed at the Rate of 6 Gallons Per Square Foot Per Minute

in satisfactory service. The reduction of pressure in a 6 foot bed is not as great as might at first be supposed. Complete statistics on this point have not been worked out, but a certain installation having a bed 6 feet 7 inches deep and 9 feet in diameter, operating under an initial pressure of 70 pounds per square inch showed, when passing 21,600 gallons per hour or at the rate of 5.34 gallons

per square foot per minute, a loss of 4 pounds pressure across the softener. When the rate of flow was increased to 31,800 gallons per hour or 8.13 gallons per square foot per minute the pressure loss was 8 pounds.

The water required for back washing, making up salt solutions and washing the bed free from salt should amount to about 4 per cent of the amount of water softened. The time required for reconditioning varies with sizes and designs, but as far as Doucil is concerned a period of 20 minutes in actual contact with the salt is sufficient and five to fifteen minutes only are needed for washing.

There is little advantage in using grains of smaller size than 30 mesh as these are capable of developing maximum capacity.

Other uses of Doucil have been considered but await development. There are numerous processes in the chemical industry where solutions other than natural waters can with advantage be freed from calcium or magnesium without suffering from the introduction of equivalent quantities of sodium. It is also to be remembered that by the use of Doucil which is exhausted from the point of view of water softening—that is, calcium or magnesium Doucil—sodium, potassium or other alkali metals and ammonia can be extracted from solution. Freedom from iron or other colored substance make it attractive for study in connection with the sugar industry and in the manufacture of salts in which alkali or alkali earth metals are ordinary impurities.

Doucil also has gas absorbing properties and is a very convenient agent for drying air for laboratory use.

Acknowledgment is due to the members of the staff and consulting experts of the American Doucil Company on whose work the foregoing statements are based.

STUDIES IN EVAPORATOR DESIGN—VI. EVAPORATORS FOR SALTS WITH INVERTED SOLUBILITY CURVES

By W. L. BADGER and H. B. CALDWELL

Read before Providence meeting, June 26, 1925

One of the most difficult problems in evaporator design is the evaporation of solutions of a salt whose solubility decreases with temperature. Calcium sulfate is the most familiar example of this group, and the difficulties due to it have been so universally experienced that they need no further comment. It is not so generally understood, however, that *any* salt whose solubility curve is of the same type will cause similar difficulties. The commonest cases are those of anhydrous sodium sulfate, and sodium carbonate monohydrate.

In evaporating a solution of any such substance, it is obvious that the stagnant layers of solution next the heating surface will be the hottest, and hence in them the material will be the least soluble. Since most of such inverted solubility curves are quite flat, a high degree of supersaturation (and hence a rapid rate of crystallization) cannot exist. This, together with the fact that the layer is stagnant, presents ideal conditions for crystallization in the form of hard coherent scale rather than individual free crystals. Once this layer of scale has formed, it salts out the supersaturation of the stagnant layer, and thus causes most of the solid deposited to be deposited as scale instead of free crystals.

It should be noted that this is the only mechanism by which hard, coherent scale may be formed. If other insoluble substances be present, they may be more or less included in the scale, but without a substance whose solubility curve is inverted, scale cannot form. The case of "salting" or the building of a deposit of crystals of a substance having a normal solubility curve, is entirely different, as will be shown in a later paper.

One factor involved in the design of any salting evaporator, and which may be positive in some cases and negative in others, is the heat of solution or of crystallization. Le Chatelier's theorem shows that in the case of a substance whose solubility increases with temperature, heat must be evolved when it goes into solution

and absorbed when it comes out. Hence, in the case of the substances discussed in this paper, additional heating surface has to be provided for this.

The rising importance of sodium sulfate in industry warrants a special consideration of this material. As the starting point for the digesting liquor in the manufacture of Kraft pulp it is in increasing demand. A considerable quantity is also used in glass making, where it partly replaces sodium carbonate, both because of its lower price and because of the fact that it does not evolve a gas on melting. There is a discussion of the uses of sodium sulfate in *Mineral Resources of the U. S.* for 1919 (p. 70–73) and by Cole,[1] who also discusses the enormous natural deposits of Canada.

The physical properties of sodium sulfate have not been determined as accurately as might be desired. The solubility is shown in Fig. 1.[2] The latent heat of solution is given by Berthelot and Ilosvay[3] as $+ 0.44 + 0.0526\ (t - 15)$ kg.-cal. per gram-molecule when dissolved in 100 gram-molecules of water. Pickering[4] shows that when anhydrous Na_2SO_4 is dried at temperatures up to 150° C., it has a heat of solution of $+ 0.057$ kg.-cal. per gram molecule in 420 molecules of water, but when fused it is transformed into another modification which has a heat of solution of 0.760 at 20.4° C. Berthelot and Ilosvay's figures correspond to 0.73 kg.-cal. at 20.4° C., hence they probably used fused salt. Pickering's lower figure probably corresponds more nearly to the reverse of the process going on in an evaporator. It is equivalent to about 0.75 B.T.U. per lb. of anhydrous salt, and is therefore of no practical significance in this problem.

The effect of the curve of Fig. 1 on the behavior of this salt during evaporation may be deduced from the ideas previously mentioned. While the solution is being concentrated, no special difficulties occur, except a decrease in capacity due to the density of the solution. As soon as the liquid reaches a concentration corresponding to saturation at the temperature of the stagnant film, scale will begin to form. If there is any circulation at all, some of this stagnant film will be torn off and mixed with the rest

[1] *Trans. Can. Inst. Min. Metal.*, *27* (1924).

[2] From Gay-Lussac, *Ann. chim. phys.*, *11*, 312 (1819); Berkely, *Phil. Trans.* (A), 203, 209 (1904); Tilden and Shenstone, *Phil. Trans.*, *1884*, 28.

[3] *Ann. chim. phys.*, (5) *29*, 295 (1883).

[4] *J. Chem. Soc.*, *45*, 686 (1884).

of the solution, so that at the start evaporation can continue, the concentration of the whole mass rises to the saturation point, and free crystals can form and grow. However, scale grows rapidly during this process, and in a very short time slows down the boiling; this slows down the circulation, there is less of the stagnant film

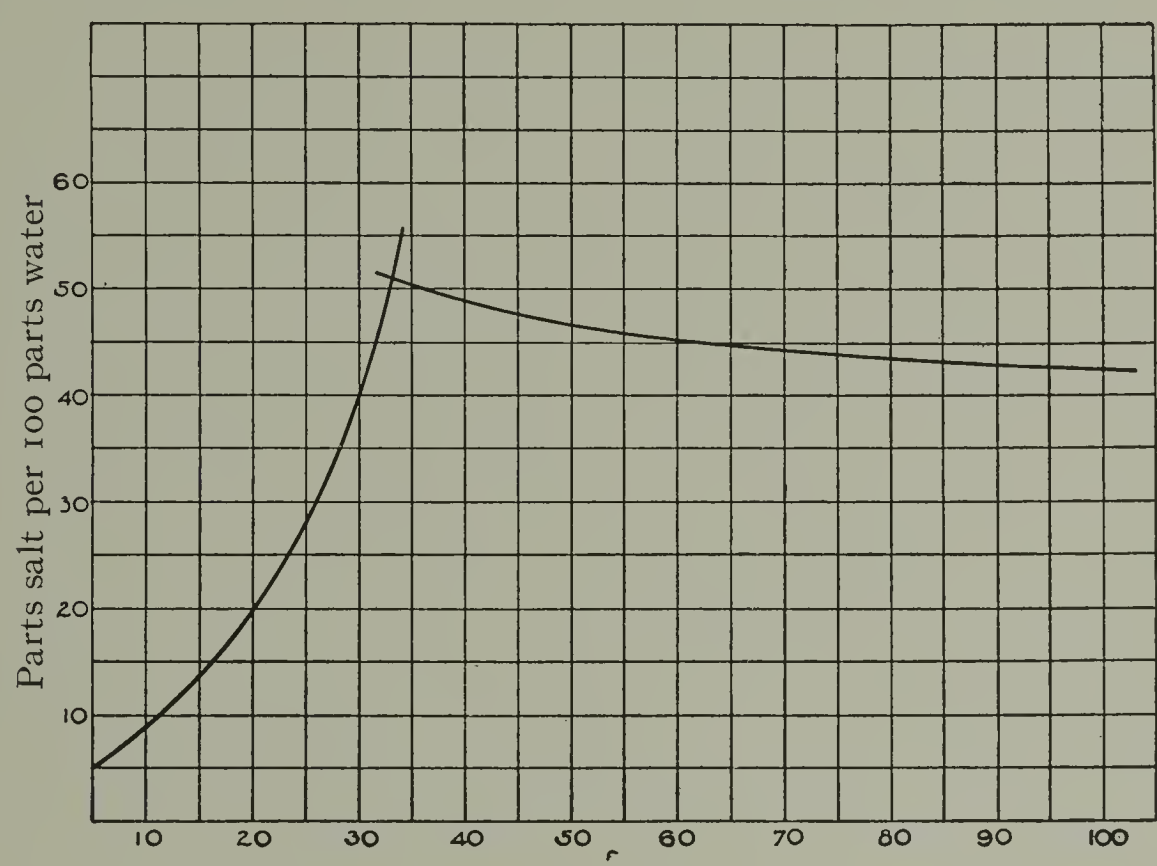


FIG. 1. Solubility of Sodium Sulphate

removed; what little evaporation there is goes to form scale, and the evaporator is very quickly so coated that further operation is impractical.

The remedy is obviously along one or both of two lines: either increase the circulation so as to decrease the thickness of the stagnant film and tear off as much of this superheated material as possible; or second, furnish a plentiful supply of seed crystals which, since the circulation will carry them into the film at intervals, will seed out the supersaturation of this film and thereby decrease the rate of scale formation. These remedies, however, will merely improve the performance of the machine. Since, even with the most vigorous stirring, the stagnant film can never be totally removed, it follows that there will always be some tendency to scale. The above methods may decrease this tendency to the point where a cycle of operation may be maintained of such length as to be commercially valuable.

At various times experiments have been carried out in the Evaporator Experiment Station to test the correctness of these conclusions. The work was all done in the vertical evaporator of the Station, which has been described elsewhere.[5] In these tests

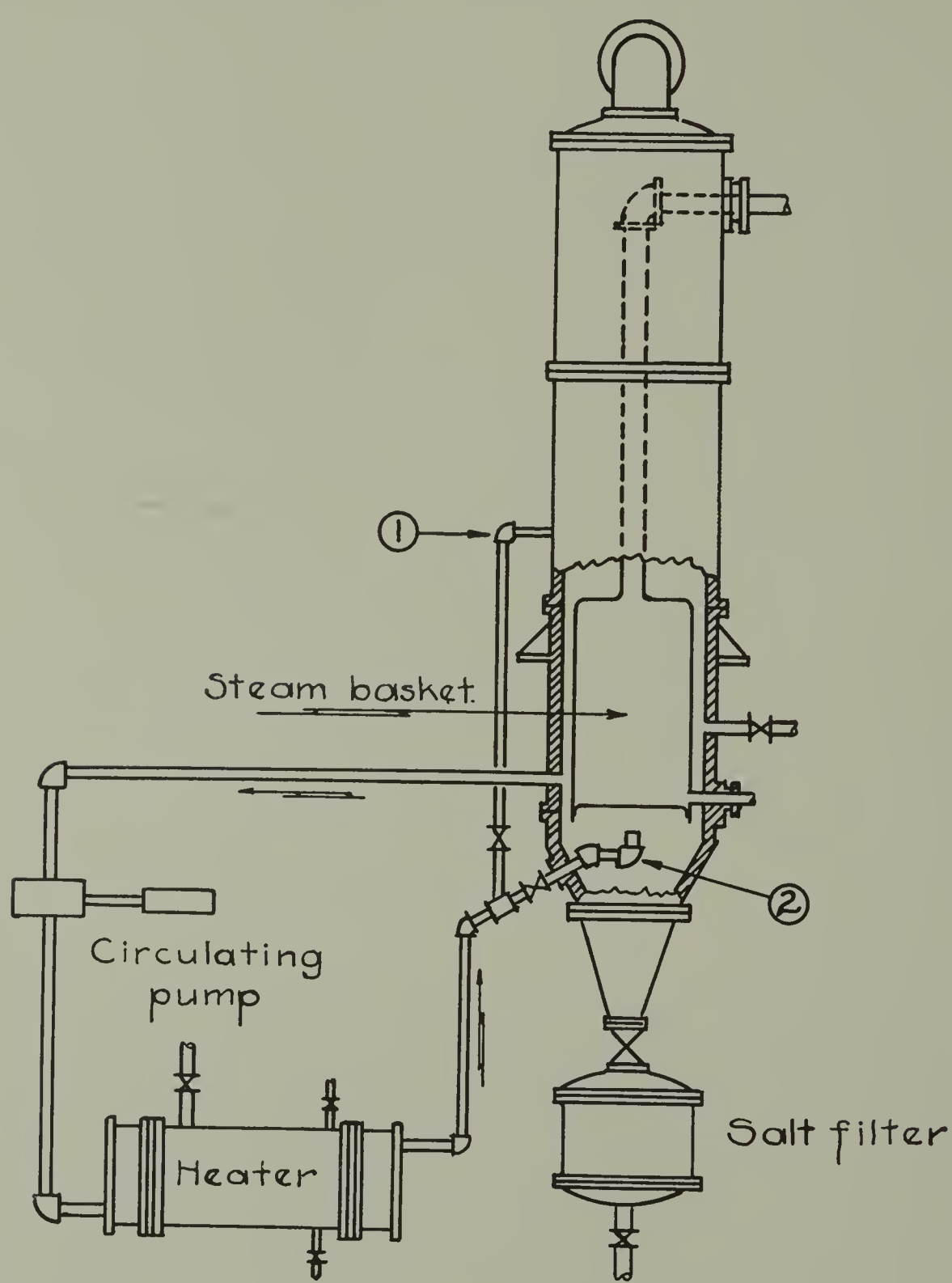


FIG. 2. Evaporator Arrangement Used for Sodium Sulphate Tests

it was fitted with a steam basket having twenty-four 2 in. iron tubes 30 in. long, making the total heating surface 43.8 sq. ft.

[5] *Trans. Am. Inst. Chem. Eng.*, *13*, (I), 77–99 (1920); *Chem. Met. Eng.*, *23*, 159–64 (1920).

In the first test the evaporator was operated in the usual way. A solution of sodium sulfate was fed at 24–26° Bé., steam was at 230° F. (6 lbs. gage) and the boiling point was 185° F. During the first few minutes after saturation was reached a few pounds of crystals were formed, but, in less than an hour, boiling had practically stopped, and a scale about $\frac{3}{8}$ in. thick had accumulated. Later, the idea was tried of supplying seed crystals by withdrawing some

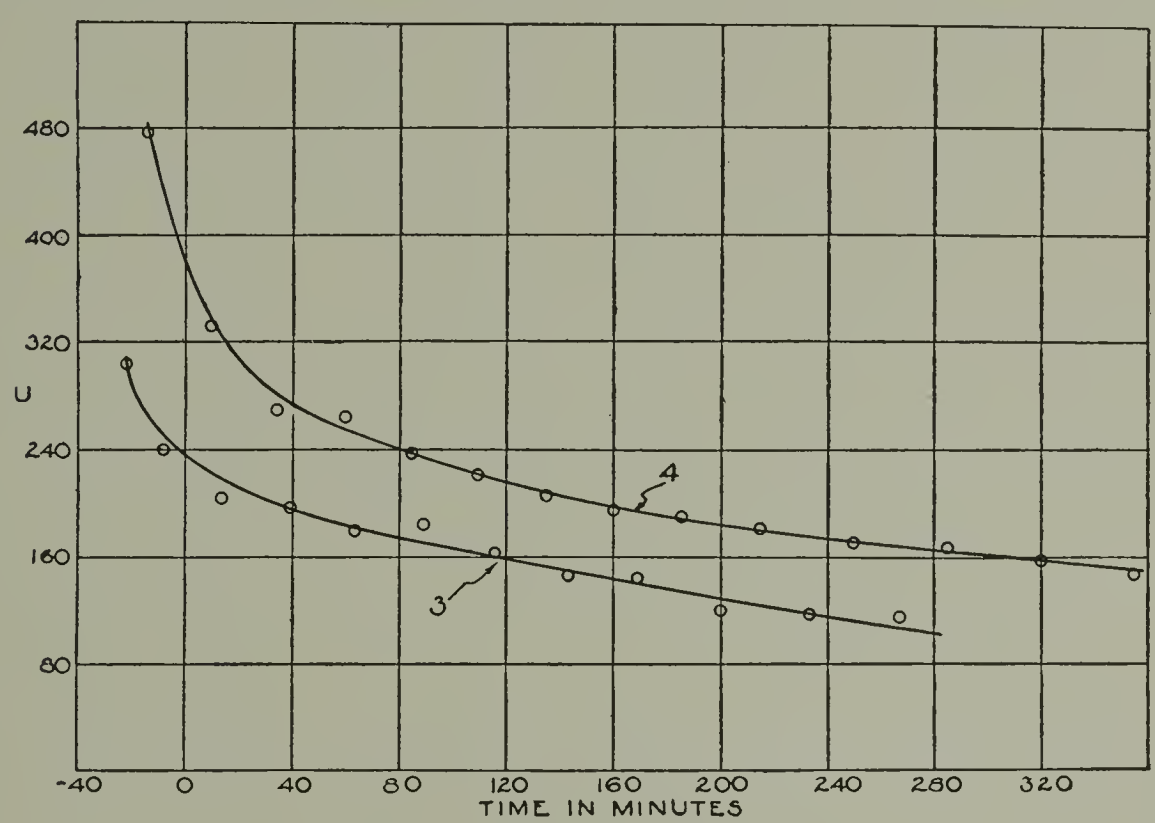


Fig. 3. Change in Heat Transfer Coefficients with Time

of the liquor, superheating it, and flashing it into the evaporator. The arrangement used is shown in Fig. 2, but pipe 2 to the bottom of the basket was not installed at this time. The flash was returned through pipe 1, above the liquor level. One result of this arrangement was that comparatively little superheat could be flashed off as otherwise the return liquor was so finely subdivided that it was carried over with the vapors.

Several tests were run with this arrangement, with and without flash. Tables I and II, and Fig. 3, show some of the results obtained. Zero time was taken as the time when crystals appeared in the evaporator, negative time is time during concentration. The effect of the supply of seed crystals in Test No. 4 is too obvious to need detailed comment.

The next idea was to return the flash *under* the basket, by pipe 2 in Fig. 2, and thus use the flash as a means of stirring as well as a

TABLE I

SODIUM SULFATE TEST NO. 3

Without Flash

Run No.	Time Since Salt	Steam Temp.	Vapor Temp.	Temp. Drop	U
19	−24	237.9	184.6	53.3	305
20	− 8	238.1	184.9	53.2	239
21	+14	238.6	184.9	53.7	204
22	+39	237.8	184.9	52.9	195
23	63	238.7	185.0	53.7	178
24	89	240.1	184.9	55.2	184
25	116	240.1	184.4	55.7	162
26	143	239.8	184.4	55.4	146
27	169	240.7	184.4	56.3	134
28	200	240.8	184.3	56.5	120
29	233	239.8	184.3	55.5	117
30	267	240.6	184.2	56.4	113
Av.		239.42	184.60	54.82	

TABLE II

SODIUM SULFATE TEST NO. 4

With Flash

Run No.	Time Since Salt	Steam Temp.	Vapor Temp.	Temp. Drop	U
31	− 14	241.0	184.7	56.3	475
32	+ 10	241.4	184.7	56.7	331
33	+ 35	241.3	184.8	56.5	269
34	+ 60	241.4	184.7	56.7	262
35	+ 85	241.3	184.5	56.8	235
36	+110	241.4	184.9	56.5	220
37	+135	241.1	184.8	56.3	205
38	160	241.4	184.8	56.6	193
39	185	242.1	185.0	57.1	190
40	215	241.8	184.7	57.1	181
41	250	241.3	184.7	56.6	169
42	285	242.1	184.7	57.4	166
43	320	241.1	184.7	56.4	155
44	355	241.0	184.5	56.5	144
Av.		241.41	184.73	56.68	

means of supplying seed crystals. Systematic tests have not been made on sodium sulfate with this arrangement, but it has been tested in the laboratory on other substances with inverted solubility curves, it has been incorporated into the design of a commercial machine for sodium sulfate, and application has been made for patents on this system.

The design of the commercial machine was based on the above data. It was a steel vertical tube basket type; having relatively long tubes in comparison to their diameter and an ample annular downtake. A double effect was used, with 2 salt filters on each effect, each having sufficient capacity for an hour's production of salt. The salt filters were fitted with large clean-out doors and manual removal of the salt was practiced. It was planned to carry a slight alkalinity in the entering liquor so that a high vapor space was provided to take care of foaming. No external catchalls were included. In most respects it was a very ordinary double effect salting out evaporator.

The most interesting part of the equipment was the patented external circulating and superheating system which greatly in creased the circulation of liquor in the tubes due to the flashing effect. The external circulation was produced by specially designed high pressure centrifugal pumps, one being used on each effect. The development of these pumps is a story in itself; but suffice it to say that considerable difficulty was experienced in the first few designs of pumps tried, due to the abrasive action of the crystals cutting away the packing and wearing down the shafts to such a small diameter that one after another would fail. These pumps were fed with liquor from beneath the false bottoms of the salt receivers. They forced it through the superheater and into a distributing nozzle beneath the center of the steam basket.

The superheater was designed to operate on high pressure steam and heat the liquor to a temperature considerably above that maintained in the body of the evaporators. Three sets of heating surfaces were provided, one for each effect and one as a spare to be used while one of the others was being washed out with water. It should be noted that these heating surfaces must be of different sizes, as the liquor being circulated from the first effect had to be heated to a higher temperature than the liquor from the second effect, in order to produce the same violence of flash in both effects. All the heating surfaces were in the same shell and heated by steam at the same pressure. While it is true that the liquor from the first effect entered the heater at a higher temperature than that from the second effect, yet the mean temperature drop between the steam and liquor is less in the case of the first effect than in the second effect. The nozzle through which the superheated liquor entered the evaporator was so designed and located as to distribute

the flash uniformly over the bottom tube sheet of the basket. Such a system would not be possible with a central downtake design of Calandria. A steam pressure regulating valve was used on the heater and a system of valves and piping was arranged so that the spare heating surface could be thrown into either the first or second effect circulating system and the heating surface thus cut out could be washed with water without interrupting the circulation.

As stated above, the anhydrous sodium sulfate crystals were collected alternately in one of the two salt filters provided for each effect. These were readily retained on the perforated false bottoms and dried to about 8 or 10 per cent moisture by blowing with steam and air. Further drying by this method is possible but the time consumed is too great. At this moisture content the salt is in a good condition for raking and is readily removed through the large square manhole with an ordinary garden hoe. For large tonnages other methods are devised to eliminate this salt handling labor.

In the design of such an evaporator, every precaution must be taken to prevent the freezing up of the pipe lines. Drain valves and steam jets must be generously provided. Plug cocks of the lubricated type gave excellent service. A special liquor level gage that would not freeze up was designed and proved very satisfactory. In this work it is absolutely necessary to maintain the static liquor level at a given place with but little variation.

After the greatest care in the design and erection of this evaporator, there were many kinks to be worked out during its initial operation. The first difficulty encountered was to maintain the circulating pumps in operation. The above mentioned abrasive effect of the crystals in suspension in the liquor proved in short order the shortcomings of the ordinary design of centrifugal pumps to withstand this terrific duty. Impellers, shafts, bearings, packings and the direct connected motors all failed. A design incorporating belt drive, extra large impeller and shaft, extremely large oil ring bearings, a long running fit casing between impeller housing and stuffing box, circulating fresh water around the shaft in front of the packing by means of a water-sealed gland arrangement and a special grade of packing solved these difficulties. With these special pumps, their attention became negligible. The circulation they helped to produce was tremendous and the flashing within the evaporator bodies sounded not unlike thunder.

After the pump difficulty, the evaporator was operated much like any double effect salting equipment. Liquor was fed into both effects simultaneously and each produced the same amount of salt. During this period an average pressure of about 10 pounds gage was maintained in the steam basket of the first effect and about 24 in. vacuum in the vapor space of the second effect. An excellent salt was produced in the first effect which was readily dried to 8 to 10 per cent moisture by steam and air blowing, but only on rare occasions was such good fortune experienced in the second effect. The salt from this effect simply could not be dried in the filters to a rakable condition. It was always a sloppy mass which would simply pour out of the filter upon opening the door. Upon careful examination it was then noticed that the grain size of the salt from the first effect was somewhat larger than that from the second effect.

It was reasoned that the grain size was subject to the same control conditions as in any ordinary crystallization process. The three factors, namely degree of agitation of the liquor, rate of crystal formation, and concentration of the solution, are the factors generally considered to control crystal size. Obviously the first two factors were the same in both effects, but the third was not. Furthermore, the lower the concentration of the liquor the larger the crystal size; and since a higher temperature was maintained in the first effect and consequently a lower concentration due to the descending solubility curve of sodium sulfate, it seemed logical that this was causing the difference in grain size. Accordingly, new operating conditions were set up, increasing the absolute pressure in the second effect, and at the same time increasing the pressure of steam to the first effect, so as not to reduce the effectual temperature drop across the machine and thus lower its capacity. When this was done no more difficulty was encountered in drying the salt in the filters of the second effect, to a good rakable condition.

Apparently, the former fine grained salt from the second effect produced such a dense mass in the filter that it was not possible to blow the mother liquor through it by means of steam or air. If a high steam pressure were used, the mass would simply channel leaving a free passage for the steam and thus make it ineffective. This assumption was confirmed by observation. Along with the increased temperature of the first effect, a larger sized grain appeared. This elevation of temperatures was accompanied by the

necessity of a feed pump as the pressure in the first effect was then considerably above atmospheric.

Next came the problem of increasing the capacity of the equipment. Up until this time the static liquor level had been carried just a little above the upper tube sheet of the steam basket. Often times the steam supply had to be cut down due to foaming. This decreased the capacity. The foaming was overcome by a careful chemical control of the alkalinity of the entering liquor, which had been made alkaline to get rid of the iron, etc., in the nitre cake which was the raw material. It was soon found that the iron could be completely precipitated and the alkalinity kept sufficiently low to prevent excessive foaming.

Various series of tests were then made with different static liquor levels and it was found that the capacity was increased fifty per cent by simply maintaining the liquor level at the right heights—about half way up the tubes. This incidentally eliminated all foaming, it evidently being broken up by the film action in the upper part of the tubes. This question of liquor level is very important, but no rule can be laid down as it will vary with each installation. It is tied up with the specific gravity and viscosity of the liquor at the particular temperature maintained; also with the degree of circulation produced by the flashing and the dimensions of the tubes. The level carried also has its effect on the hydrostatic head and in turn upon the total available temperature drop.

Further improvement in capacity came from various refinements of operation. For example, it was found that the tubes in the heater became salted up quite quickly and this was accompanied with a diminution in circulation in the evaporator due to the less violent flashing of the superheated liquor. Eventually, it was found that the washing of these heater tubes once every hour was often enough for the best results. This frequent washing did not in anyway over-burden the operator as it merely meant manipulation of valves. Also it was discovered that the static liquor level in the evaporator itself must be accurately maintained. Too high a level caused less violent circulation and very rapid incrustation of the heating surfaces. Likewise, too low a level caused the liquor ascending in the tubes to be completely evaporated before it reached the top tube sheet and the salt simply baked on the surfaces. Automatic liquor level regulators were considered but were not

installed due to the ease with which the solution would freeze upon cooling. Manual regulation did not prove difficult after the tricks were learned. The correct method in changing from one salt filter to the other empty one did much toward facilitating the maintenance of the given liquor level.

One of the greatest increases in production was due to the determination of the correct length of operating time between boil-out periods. It is to be remembered that this patented artificial circulation and superheating and flashing system did not entirely prevent the salting up of the tubes. It merely delayed it for a sufficient length of time to make the operation of the evaporator a commercial success. Many tests were made over 24 hours and longer periods of operation in which salt production was plotted as ordinates against time as abscissae. They all showed a good steady production for the first few hours but with a gradual descent to the curve. Then it would fall off quite rapidly to a low asymptotic production which would continue until the machine was dumped and boiled out with fresh water or dilute liquor. After all conditions of operation could be held constant, these curves began to fall along the same line. Then it was possible to calculate the optimum length of operation period assuming a definite time required for boiling out. This optimum operating period was of necessity modified by other features of the process such as steam consumption for boiling out, labor shifts, drying the salt in the filters, etc. However, the correct proportioning of time to the various operations did much toward increasing the daily production.

The proper control of boil-out conditions increased the production and decreased the steam consumption. It was found that dilute liquor not exceeding a certain maximum concentration was just as effective for removing the salt from the tubes as was fresh water. Also it was necessary to determine the minimum boil-out time commensurate with maximum daily production. Eventually, it was worked out that the boil-out could be satisfactorily accomplished in $1\frac{1}{2}$ hours and that two boil-outs in 24 hours were necessary. Thus 21 hours of actual salting out time was available.

It was somewhat surprising to find that during the boil-out over a ton of salt was removed from each effect. The diameter of the bodies was $6\frac{1}{2}$ feet. This boil-out liquor was, of course, saved. From these figures it is readily understandable why the heat transfer coefficients became low toward the end of a run.

This above described machine was not by any means perfect but the results obtained far exceeded any similar installation. For example, there is a machine operating to-day on sodium sulfate solutions of the same density as employed in the evaporator just discussed. It is a Calandria type with central downtake and almost exactly the same area of heating surface. The ratio of tube length to diameter is not the same nor does it employ any external circulating and super-heating system. However, the two bodies are run as single effects instead of double effect as employed in our case. The temperature drops of each of their effects is about the same as the total drop across both of our effects. Comparing capacities our evaporator produces 300 per cent of their daily tonnage. In both cases these are actual routine operation figures and they merely show how much has been accomplished by increasing the circulation. Furthermore, bear in mind that this circulation was not accomplished at any enormous expenditure of power for pumping, but simply by the utilization of part of the heat at a higher temperature level which would be consumed in any event for the evaporation.

One feature that can be improved upon in certain future installations is the method of handling the salt. Instead of being partly dried in salt filters with false bottoms and raked out by hand labor, a magma of the salt and mother liquor can be dropped directly from salt receivers having cone shaped bottoms into centrifugals. By this method it is possible to bring the salt to 5 per cent or less of moisture against the 10 per cent obtained by blowing with steam and air in the filters. If the salt is to be dried further in a dryer as for glassmakers, the centrifuge method results in a considerable saving. However, if cheap labor is available, and the salt is to be used for sulfate paper mills the filter method is probably preferable. Most sulfate pulp mill operations prefer not too dry a salt in order to keep down the dusting loss in their smelters.

This method of production of anhydrous sodium sulfate from its solutions by double effect evaporation has probably a lower cost of operation than any other system. If spray drying is considered, an enormous initial expenditure for equipment is required. Also it is impossible to make use of the multiple effect evaporation principle and fuel costs are inherently higher with the exception of the case where large quantities of waste heat at a high temperature are available. Furthermore, there is the difficulty of clogging up any nozzles that may be used in the design.

For many reasons it is doubtful whether triple effect operation would ever be advantageous.

Throughout this rather informal paper it will be noticed that the discussion is qualitative rather than quantitative. This procedure was followed as it was merely intended to point out several interesting features underlying the evaporation of salts of the descending solubility curve type.

Acknowledgments are due to the Swenson Evaporator Co. for funds for carrying out the experimental work, and for information on the operation of the commercial machine.

STUDIES IN EVAPORATOR DESIGN—VII. A GLASS AND STONEWARE EVAPORATOR

By W. L. BADGER and F. C. CUTTING

Read before Providence meeting, June 26, 1925

Most of the really acid resistant materials are difficult to work up into any standard evaporator design, so that the concentration of corrosive materials is carried out either in highly specialized equipment or not at all. The problem was brought to the attention of the writers through attempts to concentrate orange juice. This is not usually considered a highly corrosive material, but citric acid attacks all the common metals more or less. It is possible to

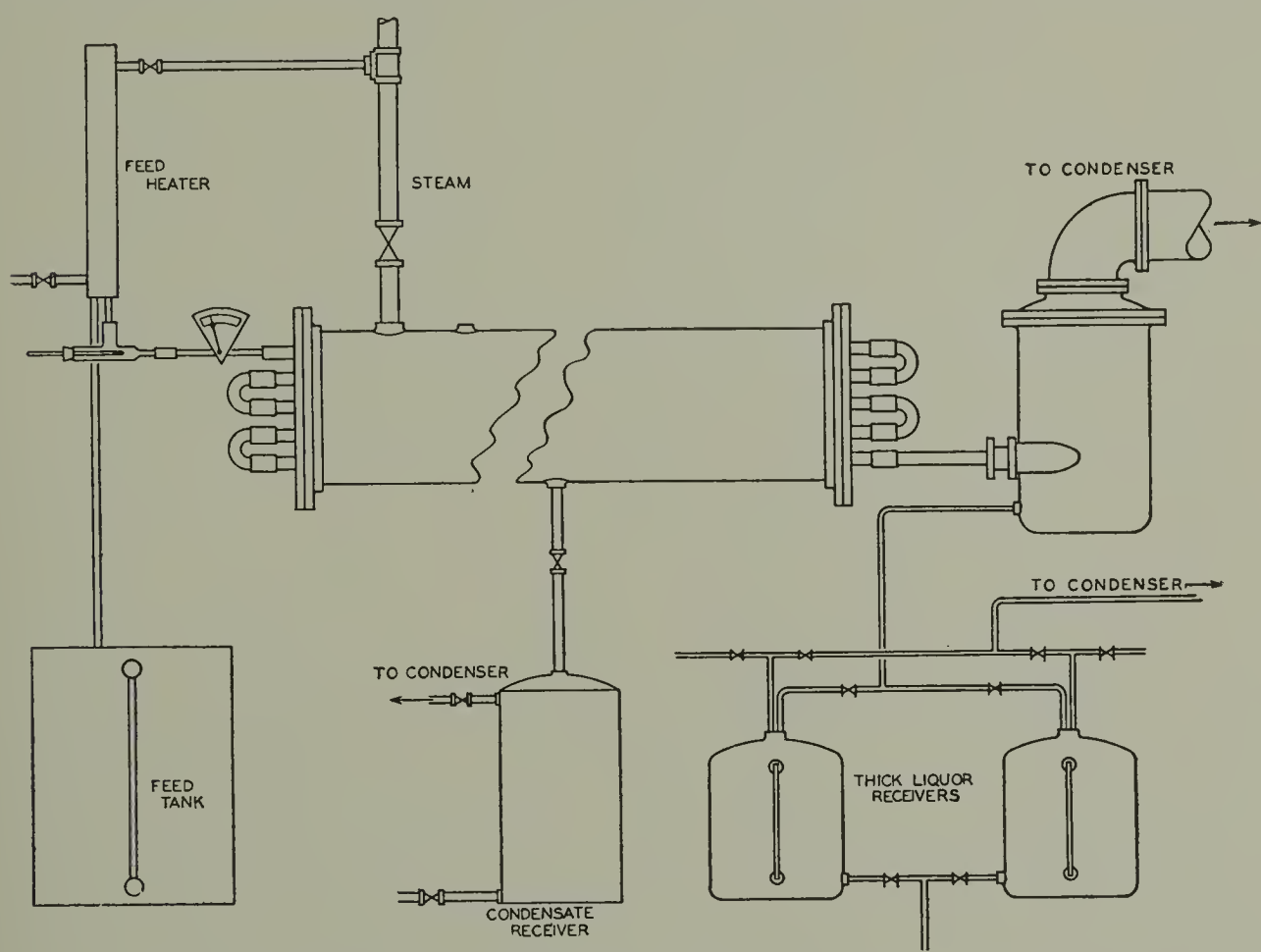


Fig. 1. Laboratory Evaporator Modified from Yaryan Design

design an evaporator with metal tubes for citrus fruit juices that will have a satisfactory life, but in this case it was desired to make a product free from traces of metals. Glass and stoneware seemed the only materials available and these were not promising either from the standpoint of mechanical properties or of heat transfer.

A laboratory evaporator was designed as shown in Fig. 1, modified from the Yaryan design. Tubes of pyrex glass, 1 in.

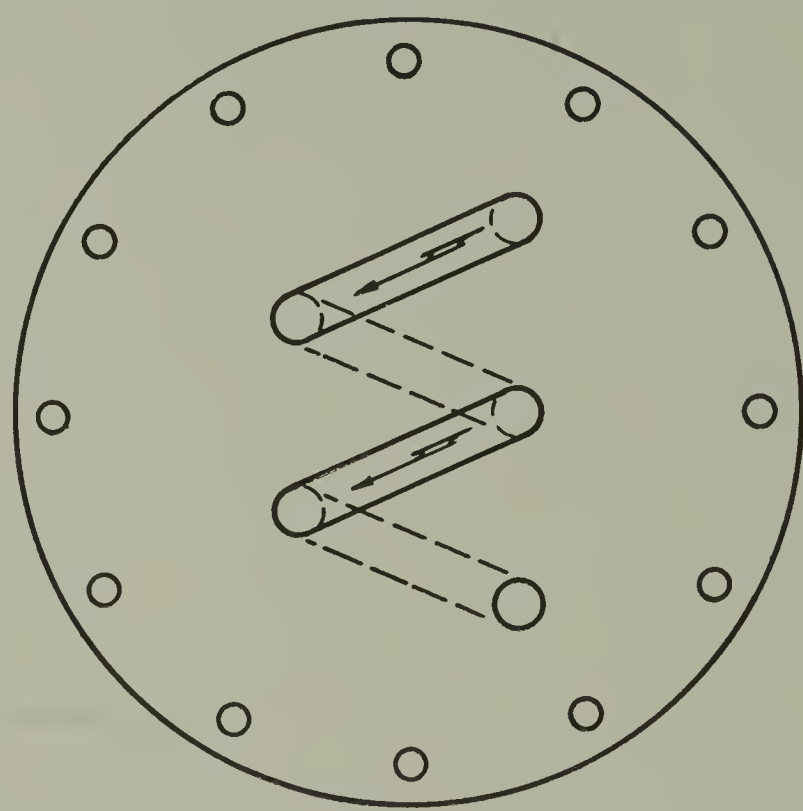


Fig. 2b.

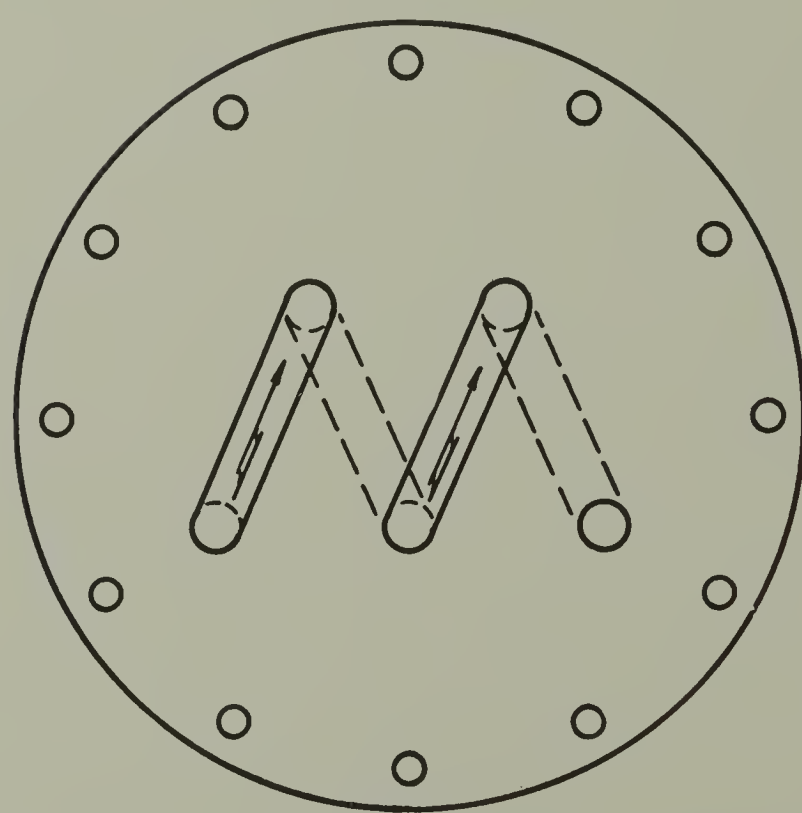


Fig. 2a.

Fig. 2. Arrangement of Tubes

o.d., $\frac{1}{16}-\frac{1}{8}$ in. wall, 130 in. long, were assembled in a steel shell made of 12 in. standard pipe. The tubes were packed into the tube sheets by stuffing boxes, and connected into a continuous coil by

pyrex return bends and rubber sleeves. The end of the coil was prolonged and packed into a stoneware vapor head through a stuffing box which entered the head tangentially. The top of this stoneware vessel was connected to a surface condenser, and from the bottom of the vessel a glass line lead to a pair of stoneware thick liquor receivers. When so assembled the evaporator had a total heating surface of 11.76 sq. feet.

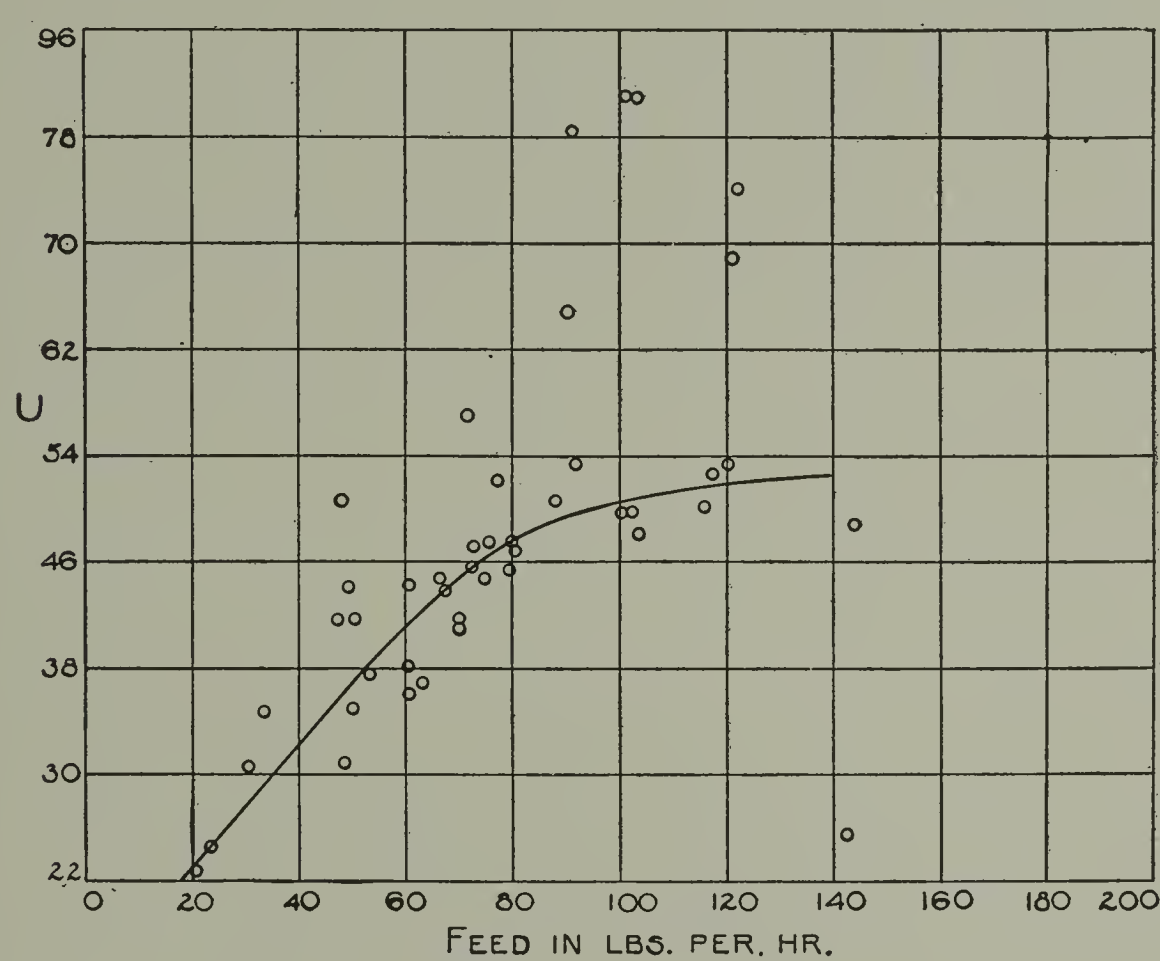


FIG. 3. Heat Transfer Coefficients, Series 1

In carrying out experiments, feed was drawn into the machine by suction, from a tank standing on scales. The thick liquor receivers were calibrated, and evaporation was taken as the difference between feed and discharge. This neglects any possible entrainment, but the work was not considered important enough to warrant investigating this error. The only surface condenser available was too small and cooling water has to be injected into the steam space of the condenser, which made direct weighing of the condensate impractical. Distilled water was used as feed, and was preheated by drawing through the heater shown.

Two different arrangements were used, as first assembled, the return bends were nearly vertical as shown in Fig. 2*b*. This made

TABLE I

PYREX EVAPORATOR

Series 1

Run No.	Vapor Temp. °F.	Steam Temp. °F.	Temp. Drop °F.	Feed Temp. °F.	Feed lb./hr.	Vapn. lb./hr.	U.
30	127.6	209.1	81.5	131.4	21.8	21.3	22.7
31	127.5	208.6	81.1	125.0	23.2	22.8	24.5
33	132.0	208.6	76.6	142.1	30.8	27.3	30.6
32	131.8	209.4	77.6	142.2	33.8	31.4	34.7
26	129.2	207.1	77.9	141.1	47.6	38.0	41.7
47	127.5	208.6	81.1	136.2	48.2	48.2	50.6
29	129.6	210.1	80.5	148.4	48.7	29.4	30.8
28	130.9	210.0	79.1	149.0	49.5	41.2	44.1
25	127.3	208.1	80.8	149.1	50.3	33.7	35.1
27	133.7	210.1	76.4	150.5	50.6	37.6	41.7
35	129.8	207.7	77.9	144.7	53.2	34.8	37.5
20	127.6	208.1	80.5	136.6	60.8	34.0	36.0
21	127.1	209.2	82.1	134.1	60.8	35.7	37.2
34	129.8	208.7	78.9	149.9	60.8	41.4	44.2
24	127.8	208.3	80.5	150.2	63.0	39.0	36.8
23	130.1	210.5	80.4	144.4	66.8	40.8	44.7
22	129.4	207.6	78.2	148.4	67.5	40.6	43.8
19	127.2	209.2	82.0	144.6	70.2	40.3	41.0
18	124.5	206.6	82.1	147.4	70.2	40.7	41.7
11	137.9	211.4	73.5	156.2	71.7	49.8	57.1
37	126.5	207.0	80.5	147.7	72.3	43.7	45.6
12	132.0	210.6	78.6	154.0	72.9	44.3	47.2
43	128.2	208.2	80.0	156.8	75.0	43.4	44.8
36	126.9	205.4	78.5	153.8	75.9	44.8	47.5
44	127.8	208.4	80.6	156.2	77.3	50.5	52.1
17	130.0	210.8	80.8	155.0	79.6	44.2	45.4
42	127.1	208.2	81.1	137.9	79.9	45.3	47.6
41	126.2	210.2	84.0	141.4	80.6	44.6	46.8
46	127.5	208.9	81.4	144.5	88.0	48.9	50.6
9	138.1	211.6	73.5	155.7	90.8	58.2	64.8
10	136.9	211.3	74.4	152.1	91.2	69.0	78.4
45	127.0	208.5	80.6	150.2	91.9	51.6	53.4
39	128.0	207.4	79.4	136.4	100.4	46.3	49.7
8	134.4	210.6	76.2	157.3	101.2	73.7	81.1
38	128.0	206.2	78.2	142.3	102.4	46.2	49.8
7	133.0	210.6	75.6	160.3	103.2	73.3	80.9
40	128.3	206.3	78.0	130.2	104.0	43.5	48.2
49	128.8	210.4	81.6	152.4	116.0	49.9	50.2
48	127.5	210.3	82.8	164.5	117.8	53.3	52.7
6	151.2	211.0	59.8	155.8	120.2	40.6	57.4
51	127.0	210.2	83.2	151.0	121.0	68.8	68.6
50	127.7	210.4	82.7	165.0	122.3	75.0	74.1
15	131.7	209.8	78.1	165.0	142.5	16.5	25.4
16	130.2	210.9	80.7	160.3	144.0	44.7	48.8
13	130.2	210.1	79.9	175.5	206.2	27.6	53.5
Av.	129.81	209.12	79.08	148.73			

the liquor travel down in half the bends and up through the others. Observations of the liquid in these bends showed that this hindered the formation of a uniform film, so after series 1 the machine was changed to the arrangement shown in Fig. 2*a*. As first assembled there were five tubes to a pass. Later this was changed so that only three tubes were used. The experiments were divided into series as follows:

Series 1—Runs 7–51, incl. 5 tubes, temp. drop constant, feed varied;

Series 2—Runs 73–100, 5 tubes, boiling point and feed constant, steam varied;

Series 3—Runs 107–128, 3 tubes, same as series 2 but a higher rate of feed.

The results of series 1 are given in Table I and plotted in Fig. 3.

TABLE II

PYREX EVAPORATOR

Series 2

Run No.	Vapor Temp. °F.	Steam Temp. °F.	Temp. Drop °F.	Feed Temp. °F.	Feed lbs.	Evapn. lbs.	Vel. ft./sec.	U.
73	133.9	186.8	52.9	145.3	80.7	15.9	205	24.5
74	133.4	187.1	53.8	145.8	80.7	19.2	250	29.3
75	133.9	188.0	54.1	144.8	79.6	17.6	227	26.8
78	132.2	192.8	60.6	150.9	77.6	25.6	344	34.7
77	131.9	193.2	61.6	149.5	80.7	24.2	328	32.3
81	131.3	196.3	65.0	145.0	84.5	33.5	460	43.1
80	131.4	196.6	65.2	144.5	84.5	31.5	431	43.2
94	130.8	198.8	68.0	140.8	82.7	36.0	501	44.9
93	130.5	199.6	69.1	144.2	82.7	36.8	518	44.8
100	131.4	201.5	70.1	144.8	84.0	37.4	513	43.8
98	131.5	202.2	70.7	145.6	84.5	37.7	515	44.6
97	131.0	202.3	71.3	142.5	90.0	40.7	565	48.0
99	131.1	202.4	71.3	146.9	81.9	42.4	585	38.3
90	130.4	202.6	72.2	147.1	78.8	34.4	484	39.9
91	130.0	202.6	72.6	145.0	77.9	29.7	423	34.1
92	129.7	202.5	72.8	144.2	81.4	43.8	628	37.8
95	130.8	208.8	78.0	140.6	82.7	42.0	585	45.8
96	130.9	209.2	78.3	144.1	80.2	40.2	558	43.5
83	130.6	211.6	81.0	147.7	82.6	40.6	569	41.8
82	130.3	211.5	81.2	145.5	79.6	37.1	523	38.4
84	129.9	212.0	82.1	144.1	81.9	40.4	575	41.6
87	130.2	214.9	84.7	147.1	79.6	41.0	580	40.7
85	129.5	214.7	85.2	151.3	77.0	40.9	590	40.1
86	128.8	214.9	86.1	146.0	78.1	41.7	611	40.0
88	130.1	224.0	98.9	147.5	78.7	46.4	657	41.5
89	129.4	224.1	94.7	147.5	78.1	45.8	662	40.7
Av.	130.96			145.70	81.18			

In this series various difficulties were met. The heater shown in Fig. 1 was not then installed and the contents of the feed tank were heated at the beginning of each run. Cooling during a run introduced a variable that could not be controlled. The thick liquor receivers were too small, necessitating short runs and hence large errors. The data show considerable variations, but give the general result of a continuous increase in capacity with an increase in rate of feed. High and scattering results were due to incomplete discharge from the vapor head due to too small a discharge line.

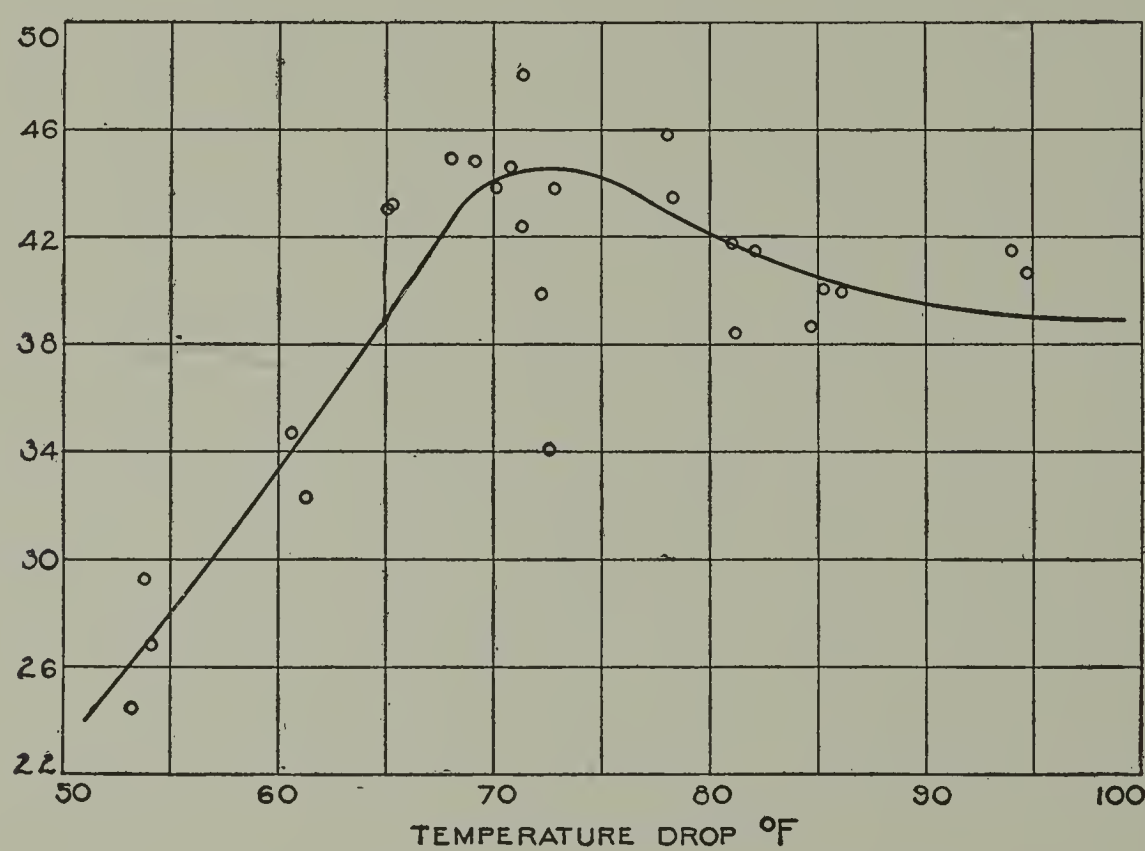


Fig. 4. Heat Transfer Coefficients, Series 2

Series 2 (Table II, Fig. 4) shows an apparent maximum in the rate of heat transfer as temperature drop increases. It should be noted that all the data in this paper are based on the *apparent* temperature drop (difference between steam temperature calculated from pressure and vapor temperature calculated from pressure in the vapor head). Due to the excessive velocities attained, the back pressure in the coils increased the boiling point and decreased the true temperature drop. The greater the apparent temperature drop, the greater this back pressure became, and hence the greater the difference between the real and the apparent temperature drops. This accounts for the falling off of coefficients at high temperature drops. This was recognized, but the magnitude of

the difference was not appreciated till six runs of series 2*a* had been made. At this point it was found that the pressure drop from entrance to exit of the coil was nearly 10 in. of mercury; hence series 2*a* was discontinued and the machine changed to a 3-tube coil.

In series 3, the heating surface was 7.00 sq. ft. Manometers were connected at each end of each tube, so that absolute pressures could be measured at these points and the pressure drop through each tube determined.

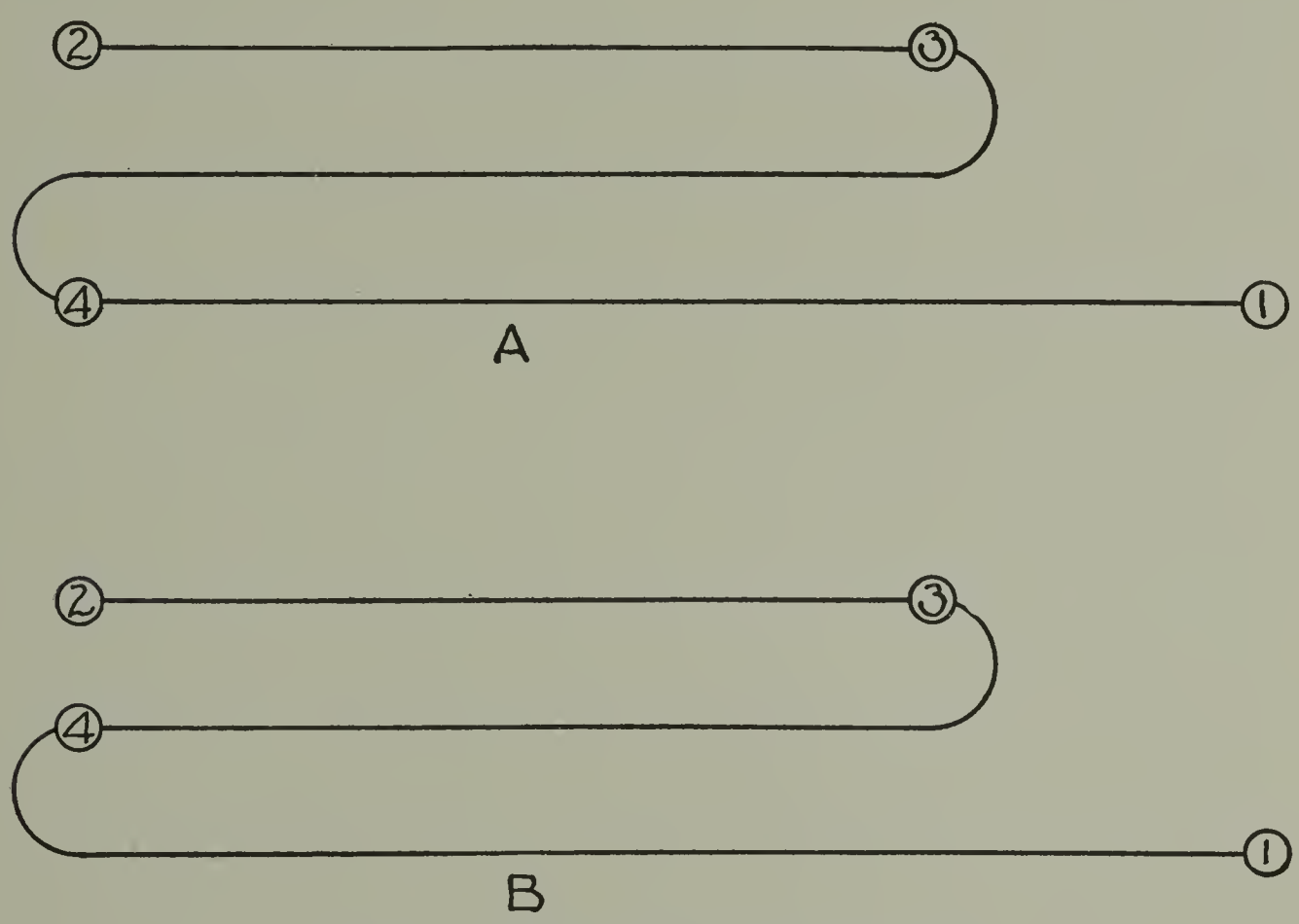


Fig. 5. Measurement of Pressure Drops

The location of these manometers is shown in Fig. 5. For runs 107–111 inclusive the manometers were attached according to diagram *A*, for the rest of the runs as in *B*. The pressure drop from manometer 3 to manometer 2 is of little significance as all these were open-arm manometers (not differential). They surged somewhat, so that the error of any one reading was possibly a millimeter.

Tables III and IV give the data, and Figs. 6 and 7 show the principal results from Series 3. It will be noted from Fig. 6 that the coefficients rise uniformly with increased temperature drop. This shows that at these rates of evaporation in a 3-tube coil, the

back pressures are not sufficient to raise the boiling points enough to affect the apparent coefficients.

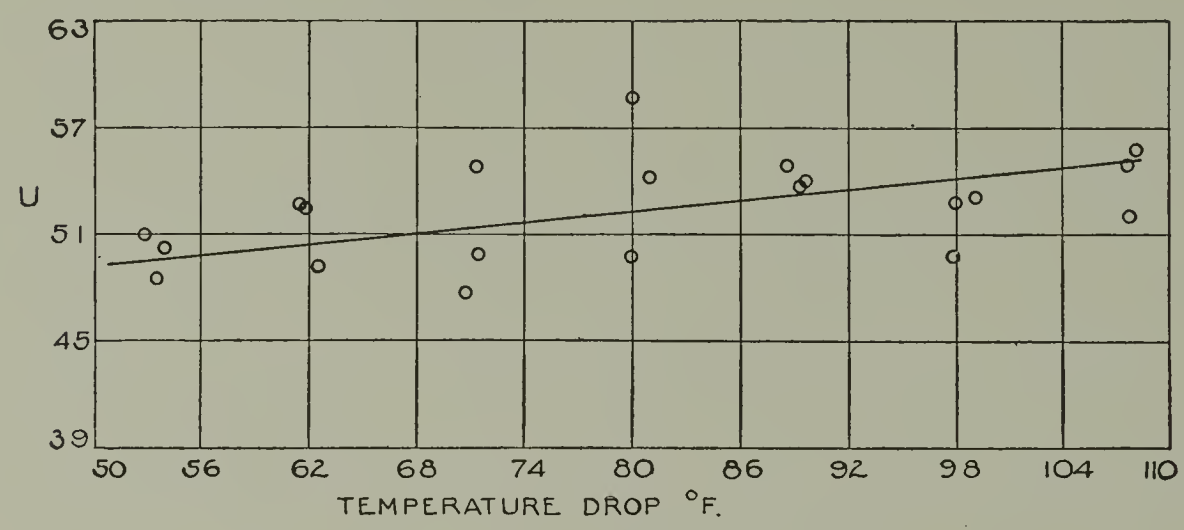


FIG. 6. Heat Transfer Coefficients, Series 3

TABLE III

PYREX EVAPORATOR

Series 3

Run No.	Vapor Temp.	Steam Temp.	Temp. Drop.	Feed Temp.	Feed lb./hr.	Evapn. lb./hr.	Vel. ft./sec.	U.
107	130.1	183.0	52.9	141.6	113.0	39.6	561	104.5
108	129.9	182.8	52.9	140.5	93.5	19.7	277	50.9
109	130.4	183.9	53.5	150.0	86.3	19.6	276	48.5
110	130.0	184.0	54.0	145.9	86.2	20.2	287	50.3
112	130.6	192.1	61.5	154.2	89.3	24.6	344	52.7
113	130.7	192.5	61.8	154.2	89.0	24.6	344	52.5
111	130.4	192.9	62.5	146.3	84.8	22.6	318	49.2
114	131.0	201.7	70.7	142.0	87.1	24.3	337	47.7
115	131.1	202.3	71.2	142.3	89.8	28 0	387	54.8
116	130.8	202.2	71.4	142.9	87.5	25 7	357	49.9
118	131.0	210.9	79.9	143.0	93.1	28 7	398	49.8
117	131.4	211.4	80.0	144.7	93.1	33 7	463	58.7
119	131.2	212.2	81.0	141.6	95.3	31 4	432	54.1
122	131.3	220.0	88.7	143.0	91.3	34.8	480	54.9
120	131.4	220.7	89.3	141.5	94.6	34.2	469	53.7
121	131.4	221.0	89.6	141.7	92.0	34.5	473	54.0
124	131.4	229.3	97.9	145.7	85.5	35.0	481	49.8
123	131.4	229.5	98.1	143.7	89.0	37.0	508	52.8
125	131.2	230.2	99.0	145.3	85.3	37.6	518	53.1
127	131.5	239.0	107.5	144.2	88.6	42.1	577	55.0
126	131.2	238.9	107.7	146.4	83.7	40.2	555	52.1
128	131.5	239.6	108.1	144.1	89.0	42.8	587	55.8
Av.	130.95			144.76	90.33			

The proportions of the tubes in this experimental evaporator were determined arbitrarily, and it may be asked whether or not they are the most desirable for commercial design. This hinges

to a very large extent on the temperature of the feed. In both Series 2 and Series 3 the feed was preheated above the boiling point, so that there was some flash at the entrance to the first tube. This greatly helped to form a film, without which the operation of evaporators of the Yaryan type is not satisfactory. When cold feed is used in a 5-tube coil, the film is formed in about the third tube (depending on rate of feed and temperature drop), so that a considerable change in the proportions of the coil will be introduced by changes in feed temperature.

TABLE IV

PYREX EVAPORATOR

Series 3

Pressure Drops

Run No.	1 to 2	1 to 3	1 to 4	3 to 2	4 to 3
107	35.3	33.9	23.8	1.4	10.1
108	36.0	33.1	25.2	2.9	7.9
109	34.6	33.1	23.7	1.5	9.4
110	34.6	33.9	25.0	0.7	9.0
111	44.7	42.2	32.5	2.5	9.7
112	44.9	42.0	33.3	2.9	8.7
113	44.7	42.4	33.4	2.3	9.0
114	50.3	48.2	38.8	2.1	9.4
115	52.4	49.7	40.2	2.7	9.5
116	52.8	49.6	40.9	3.2	8.7
117	64.8	61.3	49.2	3.5	12.1
118	66.0	61.5	51.1	4.5	10.4
119	65.9	63.0	51.5	2.9	11.5
120	68.5	66.4	53.5	2.1	12.9
121	68.7	66.4	53.5	2.3	12.9
122	68.0	65.3	52.6	2.7	12.7
123	78.6	75.0	59.7	3.6	15.3
124	83.8	79.0	63.4	4.8	15.6
125	78.0	74.3	59.3	3.7	15.0
126	91.2	87.1	70.4	4.1	16.7
127	92.3	88.4	71.3	3.9	17.1
128	93.7	88.8	72.1	4.9	16.7

If the discussion be confined to conditions similar to those of Series 3, it will be interesting to see whether the coil proportion could be adjusted to give any desired back pressure. When the total pressure drops from the vapor head to any point along the coil are plotted, Fig. 7 shows a different curve for each temperature drop.

In these experiments the vapor temperature is practically constant, and hence the density of the vapor issuing from the coil

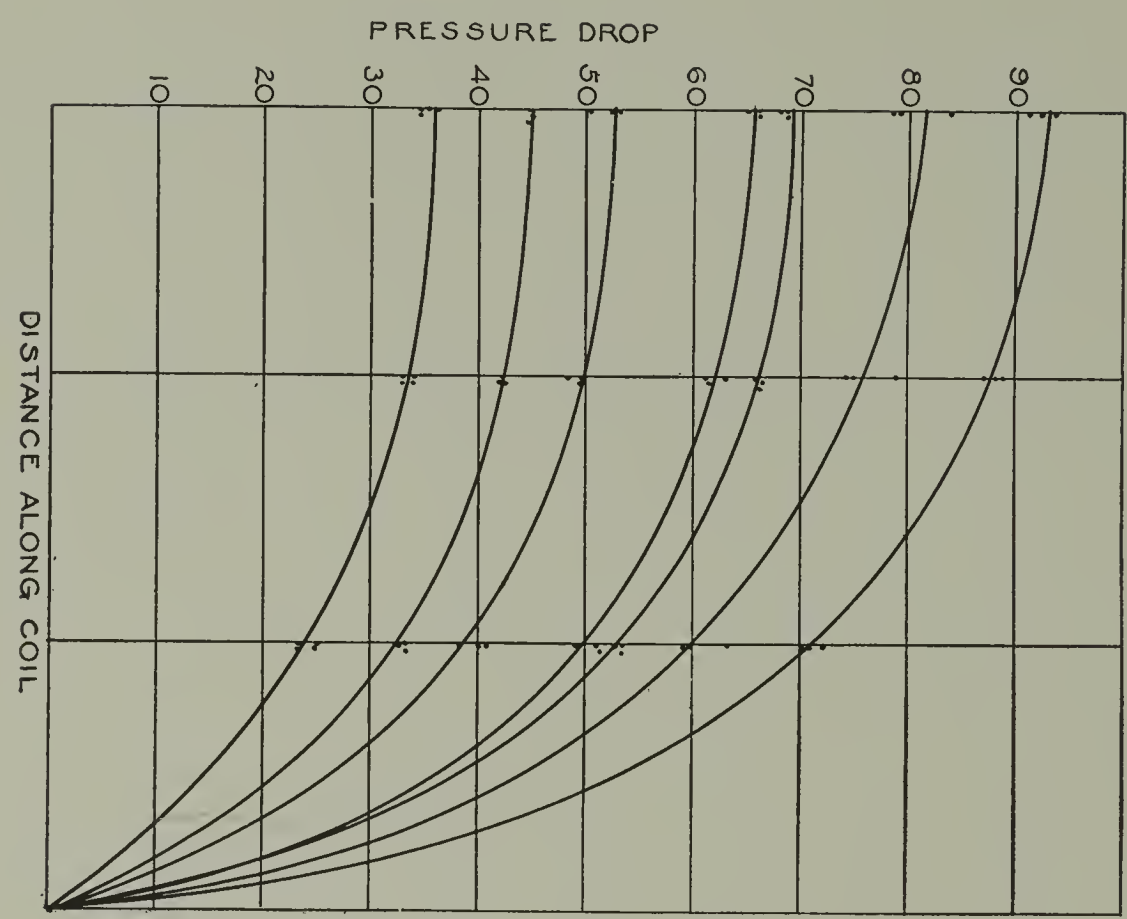


FIG. 7. Pressure Drops, Series 3

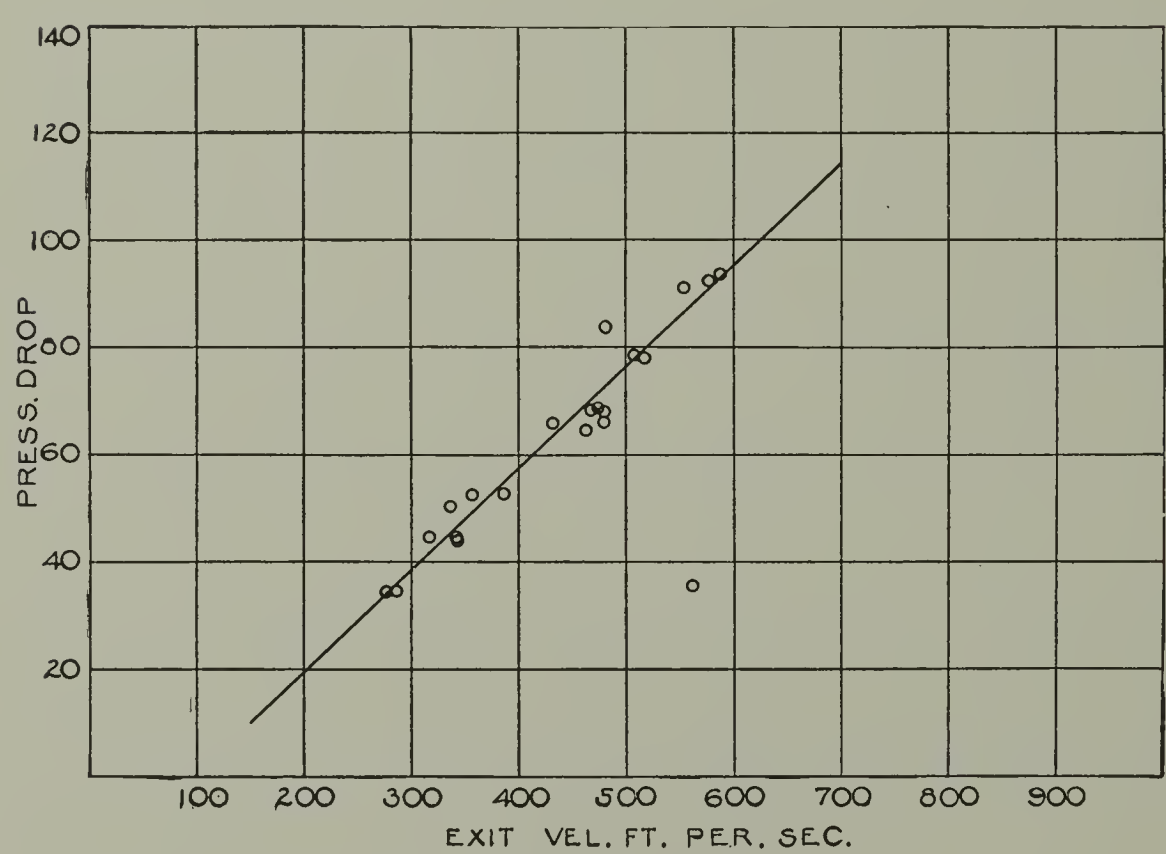


FIG. 8. Pressure Drops, Series 3

can be considered constant. The pressure drop should, therefore, be a function of the square of the mean vapor velocity. Attempts to calculate the mean velocity led to the necessity of making so many questionable assumptions that the exit velocity was plotted against the total pressure drop, with the result shown in Fig. 8. This is a much simpler relation than was to be expected.

If, then, the total pressure drop through the coil is to be held at or below any given figure, Fig. 8 shows the exit velocity which may not be exceeded. Obviously, the numerical values of Fig. 8 are applicable only to steam of the density of series 3; for other vapor temperatures and other vapor densities probably the mass velocity would be the figure which should be used. The ratio of length to diameter of the coil of this apparatus (approximately 500 : 1) would probably produce about the same pressure drop for a given exit velocity.

The coefficients obtained in this apparatus are, of course, low. The thermal conductivity of Pyrex glass is given by the Corning Glass Works as 0.0027 in metric units, which corresponds to 0.65 in English units. Since this is of the same order of magnitude as that of water (25–30 per cent greater) it is not surprising that the overall coefficient is low.

Since this experimental work was done, a commercial machine of 30 coils has been built for the concentration of dilute nitric acid. The coils are all of the same size and proportions as the experimental coil above described. It has not been in operation long enough to obtain data as to its performance, but preliminary reports say that it is operating satisfactorily.

The question of the fragility of this apparatus is raised by many who are not familiar with Pyrex. In the first six months of laboratory operation, involving starting and stopping the machine about 400 times, there were no breakages during operation. Three tubes were broken at one time or another by accident during alterations. No care was necessary in starting or stopping the apparatus; in fact, it is possible to have the machine boiling in two minutes from the time of starting.

The work discussed above was done between December, 1923, and June, 1924. In March, 1925, the machine was again used, and caused considerable trouble due to tube breakages. It is not certain at this time whether or not these breakages were due to accidental shocks, but it seems more probable that the glass has

crystallized during the year and a quarter that has elapsed. This point will receive further study.

The general result of this work has been to show that an evaporator of glass and stoneware is entirely practical, and to give certain data illustrating the factors affecting its capacity and operation.

Acknowledgments should be made to the Swenson Evaporator Co. for funds which made the work possible.

Discussion

W. A. Tuttle, Corning Glass Works (Communicated): A slight crystallization of silica appears upon the outside of Pyrex tubing immediately after drawing. In the case of the tubing used by Dr. Badger it is believed that the crystals were present before this material was originally shipped from our plant. The inside surface gave the appearance of a sort of crystallization but since this is easily removed by washing with hydrochloric acid it is assumed that this crystallization appearance was merely a scum deposited during some of his experiments. This film or scum apparently contained iron.

A. E. Marshall (Communicated): I have read with a great deal of interest Messrs. Badger and Cutting's paper on a "Glass and Stoneware Evaporator." The authors have furnished some proof of the durability of Pyrex tubes in Yaryan types of evaporators under ordinary operating conditions. The tube breakage after a year's shut down are in my opinion not due to any alteration in the physical characteristics of the glass but in all probability are due to the use of iron tubes as temporary supports and centering devices during assembly. Mr. Badger tells me iron tubes were inserted through each glass tube as an aid to locating the glass tubes in the tube sheets, and more than likely these iron tubes made a series of scratches on the inner surfaces of the Pyrex tubes, so that when heat was once more applied the tubes broke in exactly the same way as scratched gauge glasses. The use of a wooden rod should obviate this particular breakage.

Some interesting work is now being carried out on the overall heat transmission values of Pyrex and metal tubes, both at Corning and commercial tubular condenser units in various factories. The preliminary results show figures rather higher than had been anticipated, and also somewhat higher than the calculated results from Mr. Badger's evaporator figures. I am inclined to attribute this

to surfaces, glass of course being a material with a perfect surface whereas most metals build up surface films and eventually are scaled and corroded. It can already be stated as a result of some of the work, that the practical heat transmission values do not show any direct relation to the thermal conductivity values.

Dr. Badger has made reference to the use of glass tube evaporators for citric and for dilute nitric acids. Evaporators of this type should also find application in the concentration of solutions of metallic chlorides, which usually contain free hydrochloric acid and are therefore difficult to handle in standard equipment. Examples of such solutions are iron, tin, and zinc chlorides.

While the glass tube evaporator cannot be said to have reached finality in design, it is nevertheless in a forward state of development and in such shape that it can be used commercially.

STUDIES IN EVAPORATOR DESIGN—VIII. OPTIMUM CYCLE FOR LIQUIDS WHICH FORM SCALE

By W. L. BADGER and D. F. OTHMER

Read before Providence meeting, June 26, 1925

The rate of change of heat transfer in evaporating substances which form scale has been investigated by McCabe and Robinson.[1] They assume that the amount of scale present at any time is proportional to the total amount evaporated up to that time, and on this assumption derive the formula

$$\frac{1}{u^2} = a\theta + b. \tag{1}$$

Where u is the overall coefficient of heat transfer, θ is time, and a and b are constants. Since evaporators operating under such conditions must be cleaned at intervals, it is desirable to be able to calculate the optimum length of cycle.

Let X = time of one cycle in hours,
C = time for cleaning, in hours,
N = no. cycles per 24 hours = $24/(X + C)$,
A = total heating surface of evaporator,
L = heat input per pound of water evaporated,
Q = total heat transferred per cycle,
G = lbs. evaporated per cycle,
Δt = working temperature drop,
E = lbs. evaporated per 24 hours.

Solving equation (1) for u we have

$$u = \frac{1}{\sqrt{a\theta + b}}. \tag{2}$$

The total heat transmitted per cycle, Q, is given by

$$Q = Au\Delta t = A\Delta t \int_0^x \frac{d\theta}{\sqrt{a\theta + b}}, \tag{3}$$

[1] *Ind. Eng. Chem.*, *16*, 472–3 (1924).

and for the total evaporation per cycle, G, we have

$$G = \frac{Q}{L} = \frac{A\,\Delta t}{L}\int_0^x \frac{d\theta}{\sqrt{a\theta + b}}\,. \tag{4}$$

If all the constant factors on the right-hand side be combined into one constant $\frac{1}{m}$, we have

$$mG = \int_0^x \frac{d\theta}{\sqrt{a\theta + b}} = \left[\frac{2\sqrt{a\theta + b}}{a}\right]_0^x = \frac{2\sqrt{aX + b} - 2\sqrt{b}}{a}\,. \tag{5}$$

Equation (1) may be plotted from experimental data ($1/H^2$ as ordinates against time) and from such a plot the numerical values of a and b may be determined graphically. When these are substituted in equation (5) a definite numerical solution is possible, as the factors included in the constant m are all known.

In order to find the length of cycle which will give the maximum production per 24 hours, we may write

$$E = nG = \frac{24G}{X+C}\,. \tag{6}$$

Substituting the value of G from equation (5) and rearranging,

$$E = \frac{48A\,\Delta t}{aL}\left(\frac{\sqrt{aX + b} - \sqrt{b}}{X + C}\right). \tag{7}$$

In order to find the maximum value of E we may proceed in several ways: (a) we may plot equation (7) and determine its maximum by inspection; (b) we may differentiate equation (7) either directly or graphically and determine from the plot of the derivative where it is equal to zero, or (c) we may differentiate equation (7), set the first derivative equal to zero, and solve for X. Method (c) is very clumsy for this equation, and the quickest and simplest method is (a).

As an illustration we may take some data from the evaporation of hard water. The experiments were run in an experimental Yaryan evaporator having one iron tube, $2\frac{1}{2}$ in. in diameter and 50 ft. long, encased in a steam jacket. The water contained 280 p.p.m. of $CaCO_3$ and 156 p.p.m. of $CaSO_4$. The boiling point was

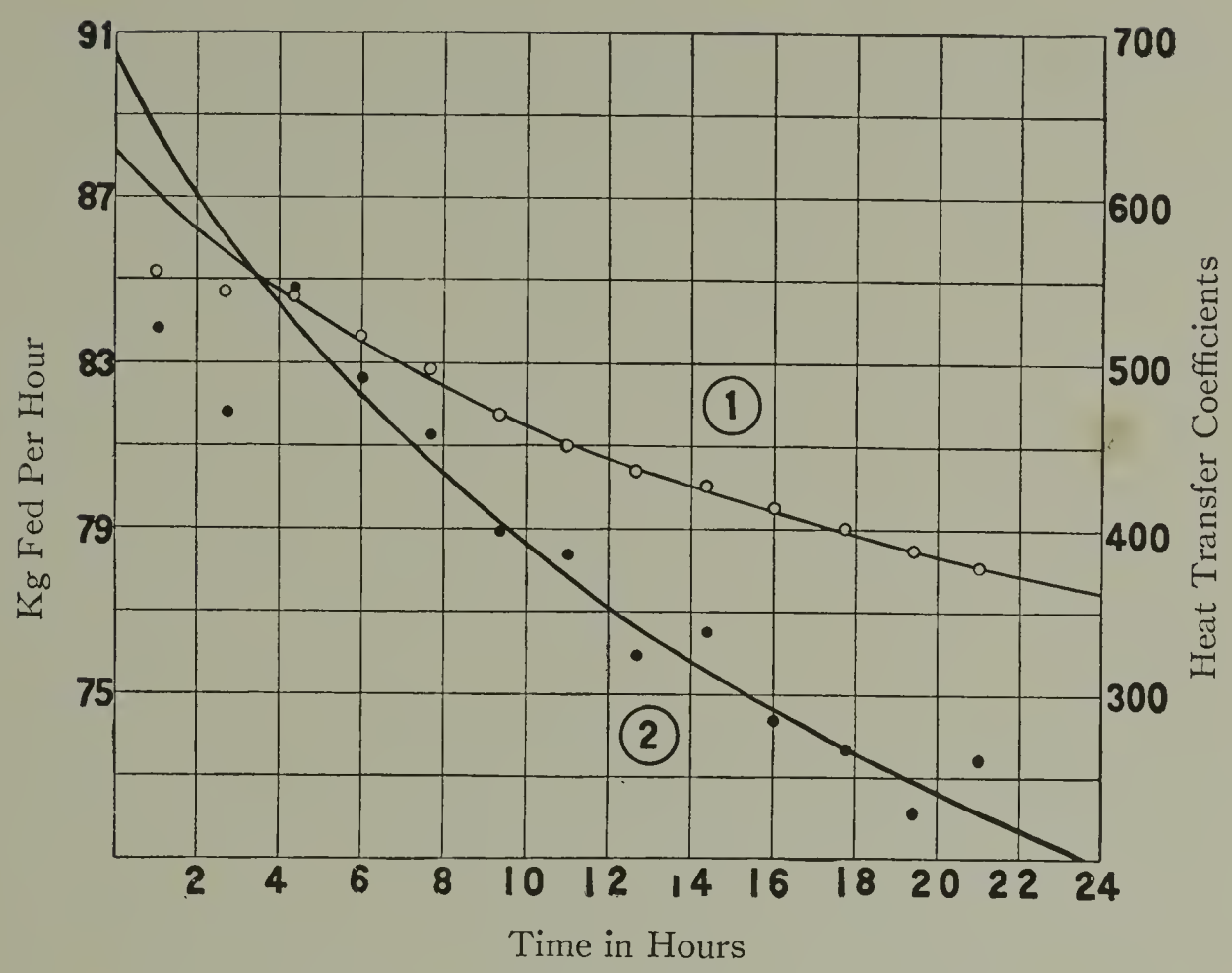


FIG. 1. Evaporation of Hard Water in Yaryan Evaporator
Curve 1—Heat Transfer Coefficients
Curve 2—Rate of Feed

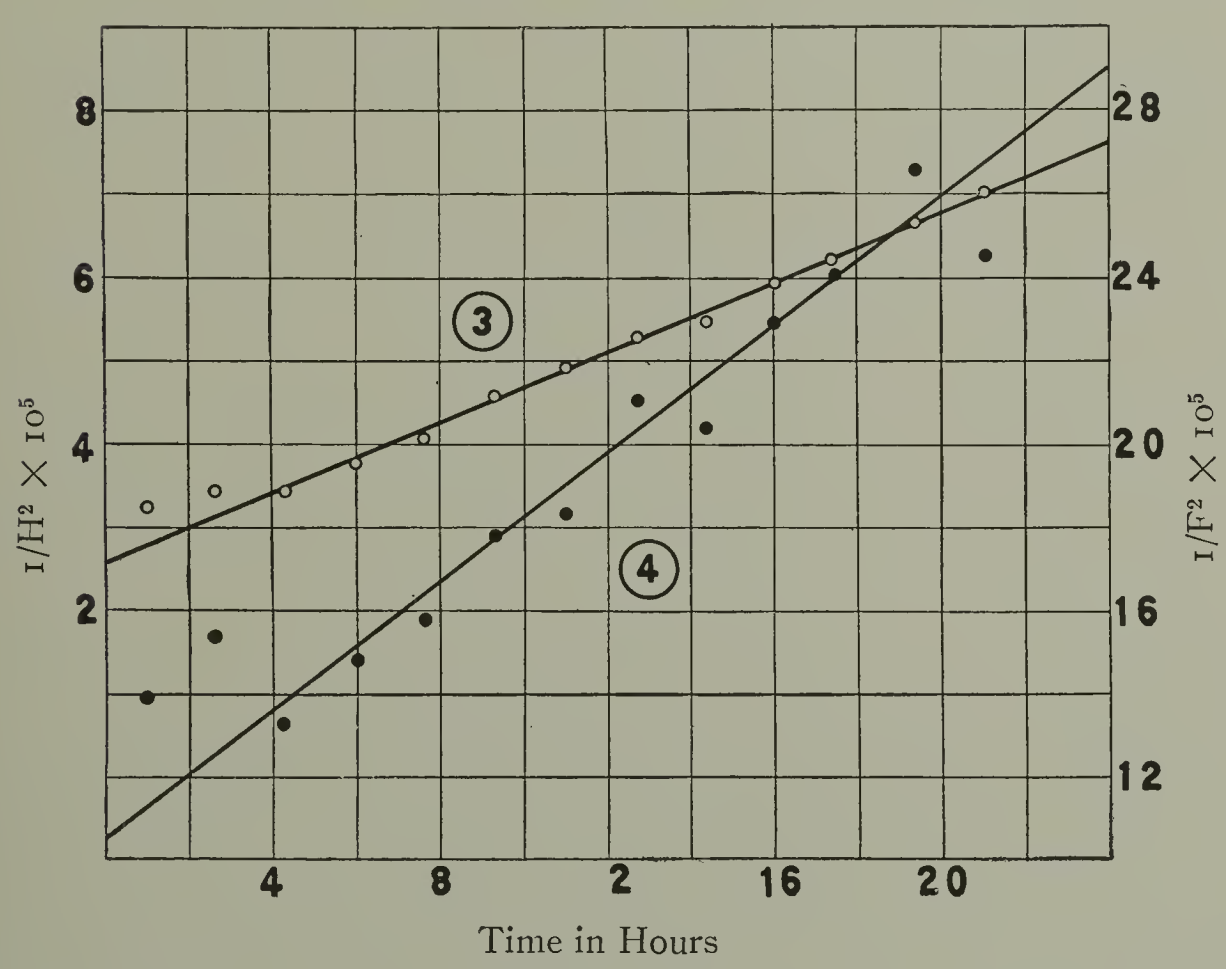


FIG. 2

210° F. and the steam temperature 286° F. Curve 1 shows the data as taken, expressed as coefficient *vs.* time. Curve 3 shows the plot of equation (1) derived from this data. From this line we find the constants of equation (1) to be

$$a = 0.212 \times 10^{-6},$$

$$b = 2.55 \times 10^{-6}.$$

Substituting in (7), assuming $h = 3$ hours and letting p equal the constant factors on the right-hand side of the equation, we have

$$\frac{E}{p} = \left(\frac{\sqrt{0.212x + 2.55} - 1.595}{x + 3} \right). \tag{8}$$

The plot of the right-hand side of this equation is shown in Curve 5, and the maximum is seen to be at 15 hours. That is, if this machine is cleaned every 15 hours the total production will be a maximum.

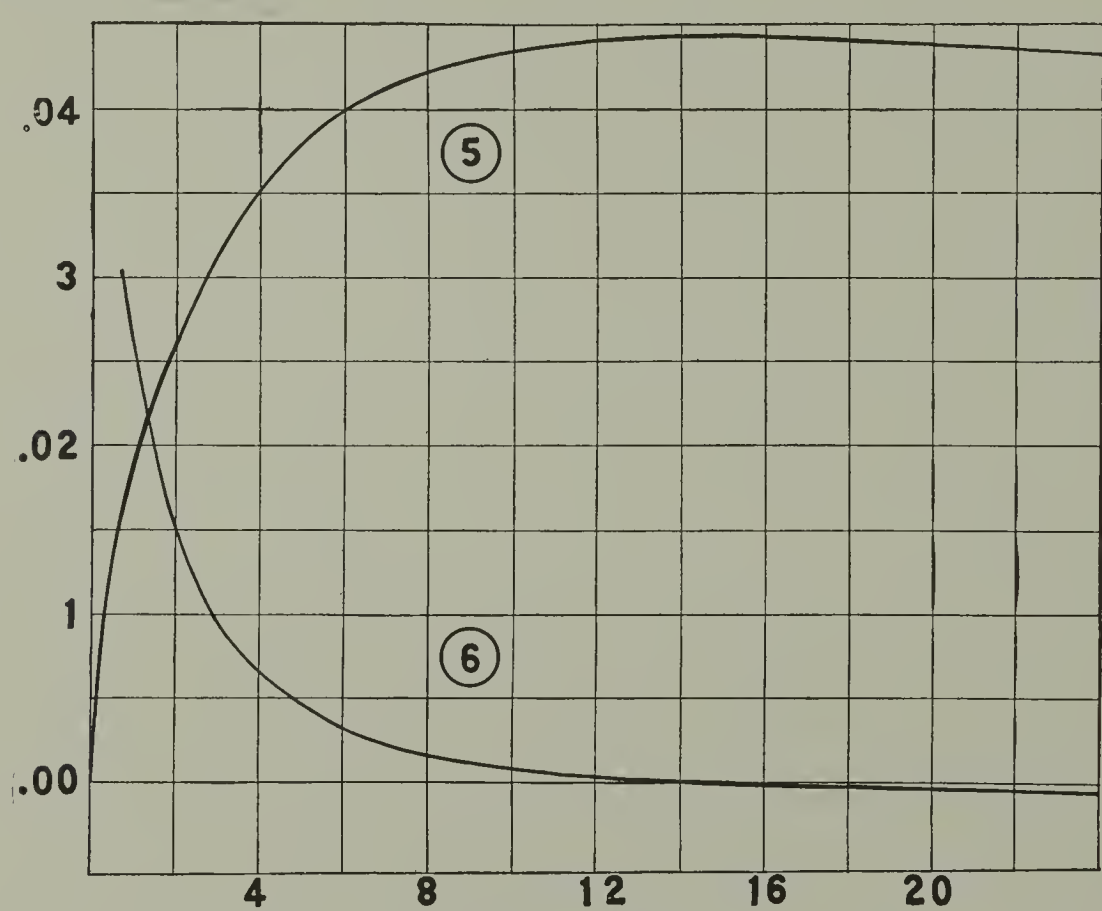


FIG. 3. Time of One Cycle in Hours

Curve 6 is a graphic differentiation of Curve 5, and this shows a value of zero (maximum production) at 15 hours. It is interesting to note the very flat portion of Curve 5 near the maximum. The total evaporation per 24 hours is not much different for cycles between 10 and 24 hours. Similar curves have been obtained for

other cases. In other words, the evaporation per 24 hours would not be greatly different whether the cycle were 12, 16, or 24 hours. Hence this machine could be boiled every 12 hour shift, every two 8-hour shifts, or every 24 hours, without affecting the capacity per 24 hours. This is a function both of the steepness of the $1/H^2$ curve and of the time for cleaning. With steeper $1/H^2$ curves and longer times for cleaning, the maximum is more plainly marked.

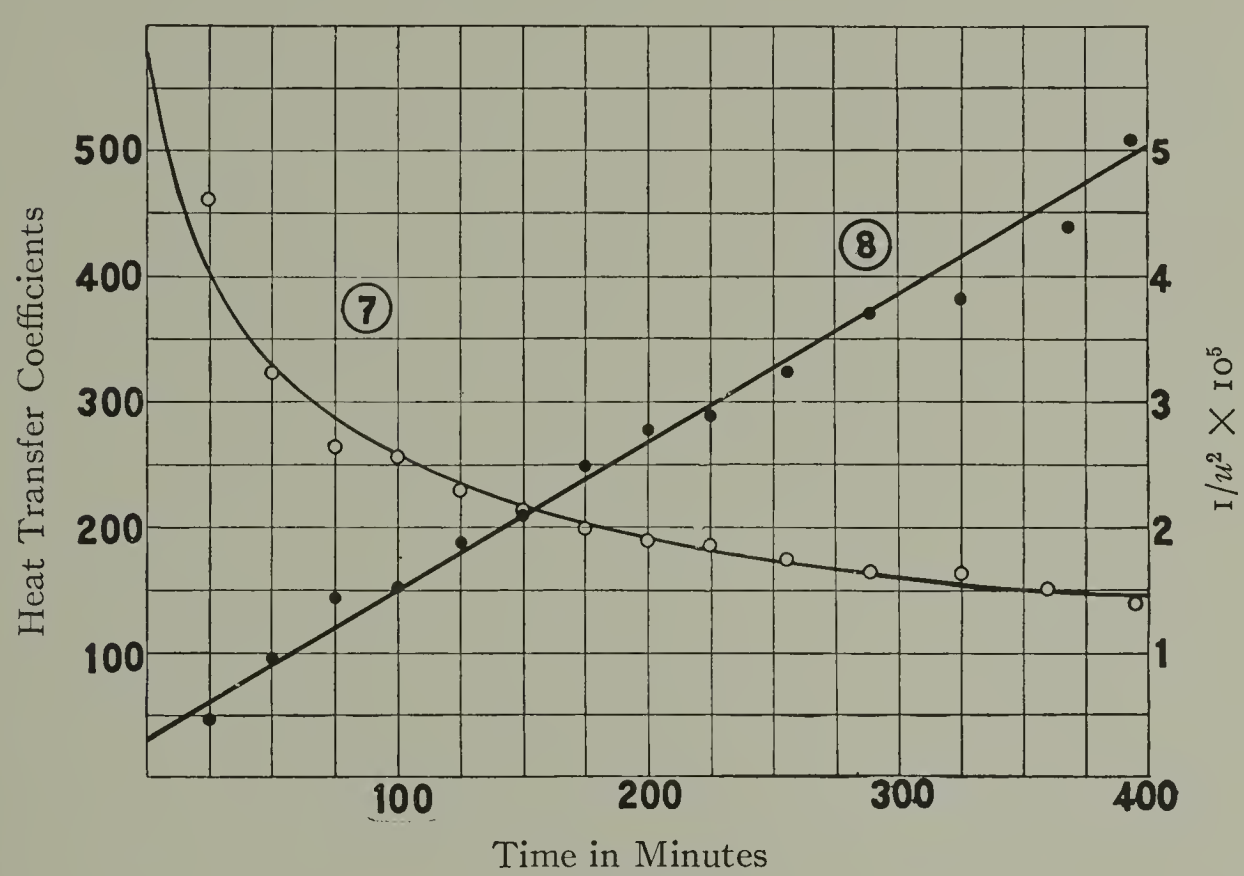


FIG. 4

In many cases in practice the determination of a heat transfer coefficient is not convenient. If the temperature drop be maintained constant, and if other factors (such as ratio of feed to discharge) remain constant, the coefficient may be taken as proportional to the feed, or to the condensate, or to any other quantity which can be measured easily and which is proportional to the evaporation. A flowmeter on the feed would probably be most convenient.

Curve 2 represents rate of feed against time for this same run and Curve 4 is the $1/F^2$ curve analogous to equation (1). Since Curve 4 is also a straight line, the constants a and b may be derived from it, and substituted in equation (8) as before. This will give the length of cycle for maximum *feed*, but since by assumption evaporation is to be a constant fraction of the feed, this will give

the maximum evaporation also. Due to variations in temperature drop and in discharge ratio, the $1/F^2$ curve will not be as accurate as the $1/H^2$ curve, but the accuracy of the integral curve will be about the same in both cases.

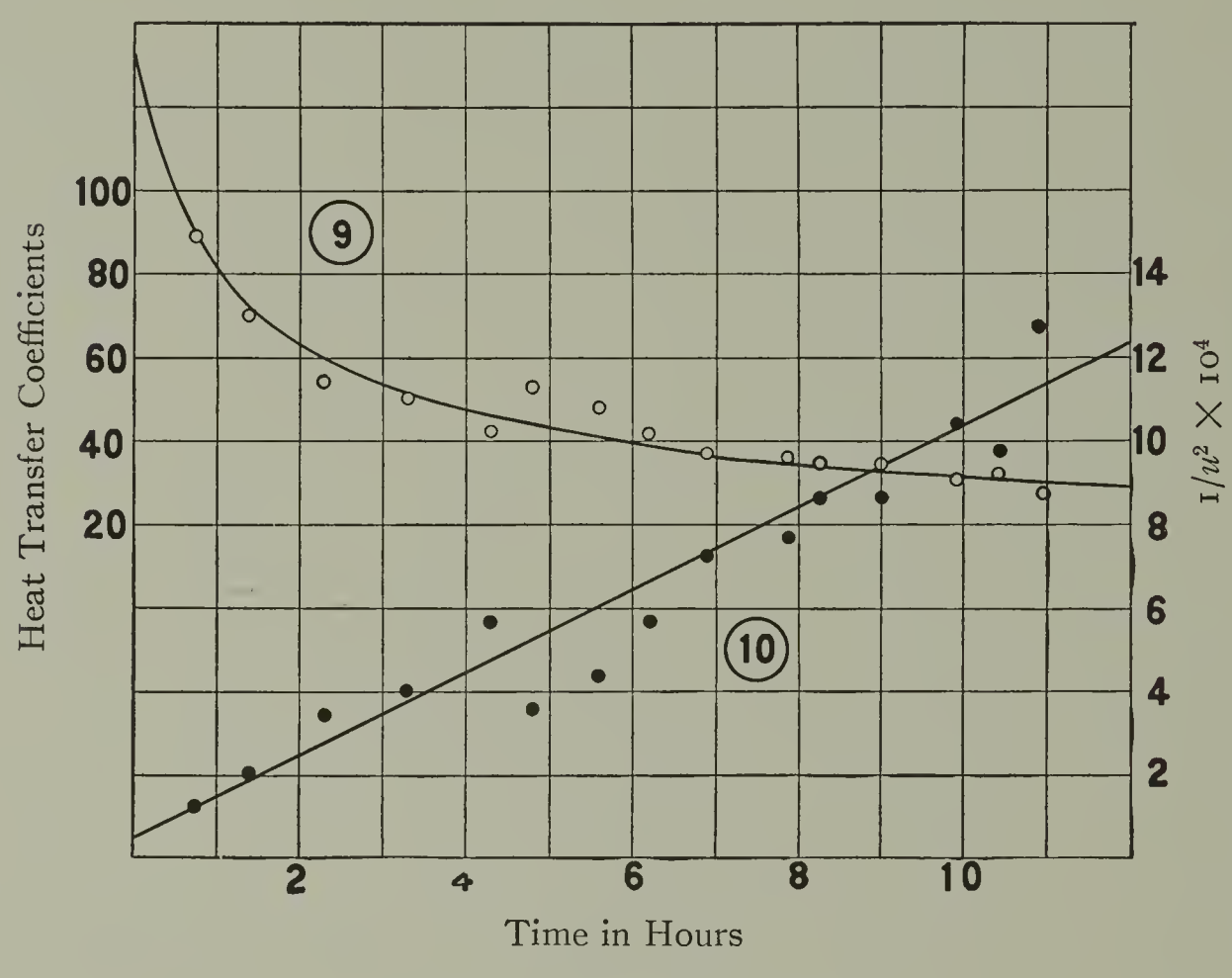


Fig. 5

Curve 7 is the plot of Test 4 on sodium sulfate from the preceeding paper. Curve 8 is the $1/H^2$ plot of the same data, showing that this obeys the assumptions on which equation (1) is based. Curves 9, 10, 11 and 12 are similar curves for sodium carbonate monohydrate, showing that this too is amenable to the above treatment. It is of interest to note that equation (1) was based on a scale so thin that the mean heating surface did not change. In these last two cases this was not true, as a very thick scale was formed before the end of the run, but a straight line still represents the $1/H^2$ curve satisfactorily.

Curve 15 is a plot of the coefficients, and Curve 16 is a plot of the values of $1/H^2$, for a run with sodium chloride, in a vertical tube evaporator with forced circulation. This shows plainly that the salting up of the heating surfaces in such evaporators is a phenomenon quite different from scale formation, and not amenable

to treatment based on equation (1). The coefficient fell off for four hours at the beginning of the run, then was constant for 12 hours, and after salt crystals began to form on the surfaces the evaporator slowed down rapidly. A number of such experiments have been carried out in the Evaporator Experiment Station, but all show the same shaped curve. The length of the flat part of the curve is partly a function of the degree of agitation, partly a function of operation. An error in operation (too high or too low a level, irregular steam pressure, etc.) may cause the salt crystals to begin to grow on the surface (and hence start the last downward slope of the curve) at almost any point in the cycle. Hence, the maximum

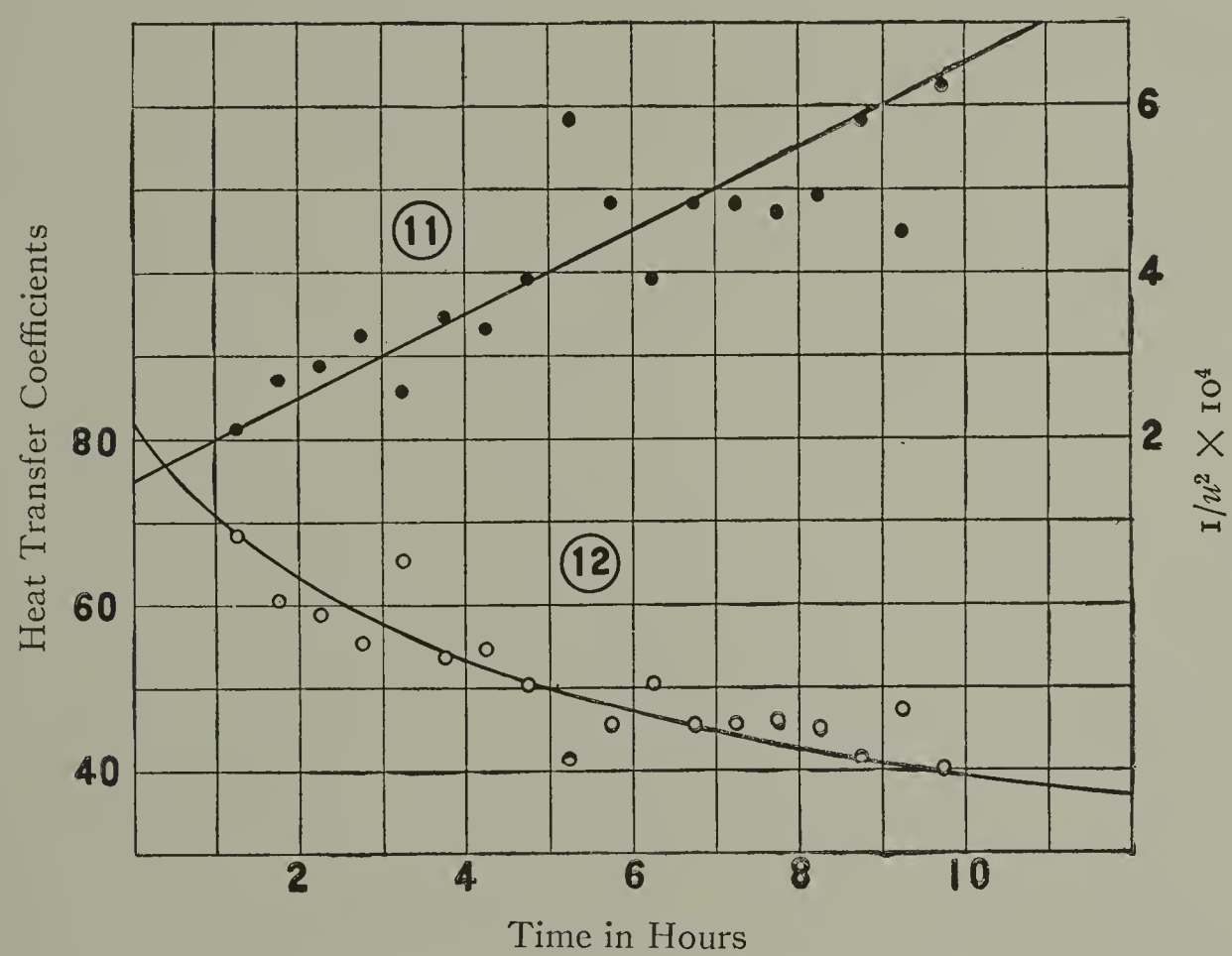


FIG. 6

capacity of a salt evaporator cannot be calculated from the above equations, and the phenomenon of "salting" is quite distinct from that of scaling.

The cycle of maximum production may not be the cycle of minimum cost. This depends on the relation of operating to overhead costs, on the ratio of boiling time to cleaning time per cycle, and on the ratio of cost per hour for labor for cleaning to cost per hour for labor for operating. Low overhead costs and high costs for cleaning tend to longer cycles, and vice versa.

If we assume that interest, depreciation, repairs, insurance, and taxes may be represented by a flat sum per day, we may make the following analysis:

Let o = overhead cost in dollars per 24 hours,
d = labor cost during boiling in dollars per hour,
e = labor cost during cleaning in dollars per hour,
f = steam cost per pound of evaporation.

Then the total cost per day is

$$o + dNX + eC + Ef$$

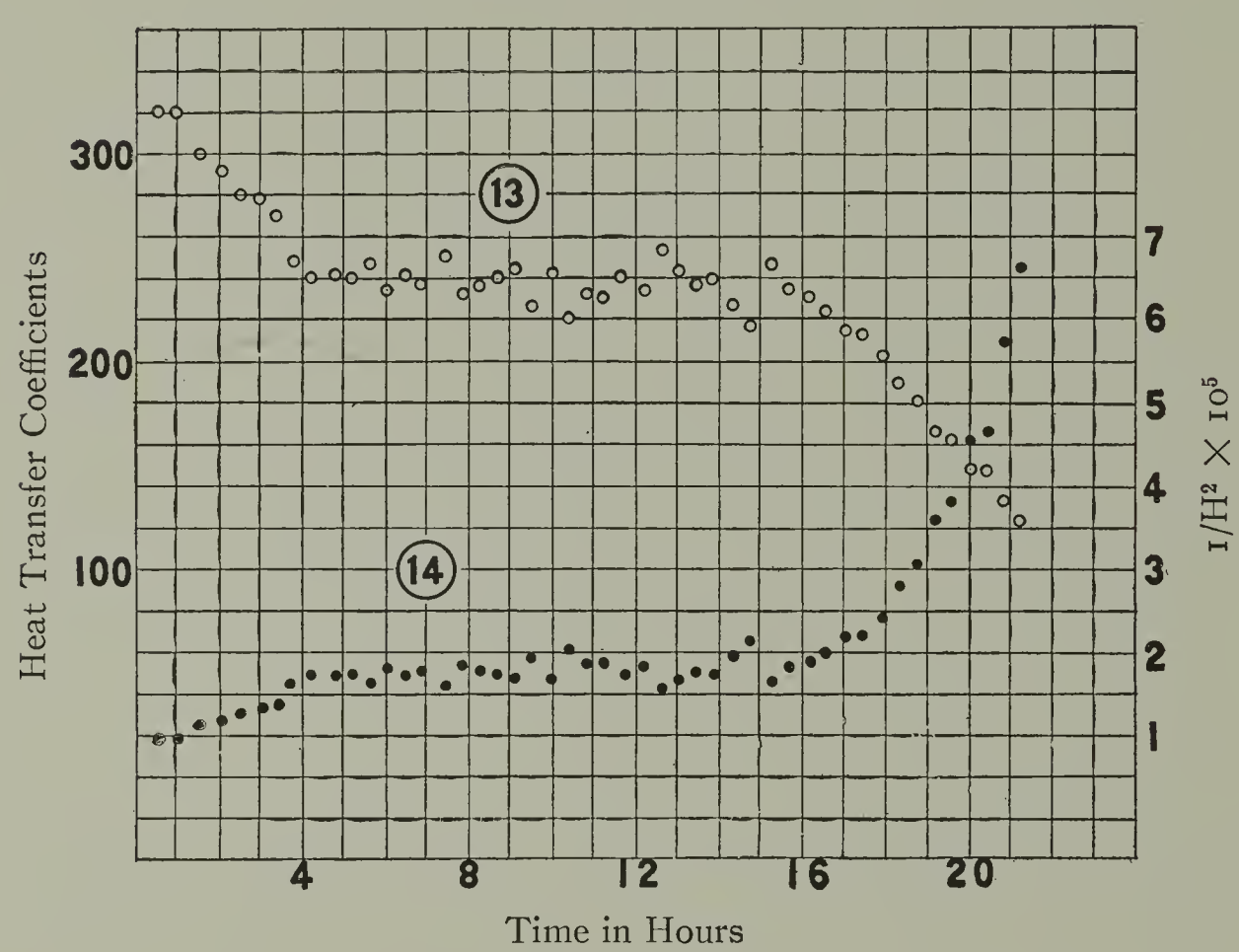


FIG. 7

and we may write

$$\text{cost per lb. evaporated} = \frac{o + dNX + eC}{E} + f. \qquad (9)$$

Substituting $\frac{24}{X+C}$ for N, and the value of E from equation (7), we have

$$\text{cost} = \frac{aL(X + C)(o + eC) + 24adLX}{48A\,\Delta t(\sqrt{aX + b} - \sqrt{b})} + f. \qquad (10)$$

This may be evaluated for any given case, plotted, and the length of cycle giving the minimum cost may be determined by inspection.

The possible variations in the actual values of the constants in this equation are so great that it has not been thought worth while to work out an illustrative problem.

Discussion

Mr. W. L. McCabe (communicated): Your paper treats of determining the optimum cycle for an existing machine. It answers the question, "How can a machine with a definite area, delta t, steam flow-sheet, etc., be operated for maximum production or lowest cost?" It seems to me that another question can be answered in the same way. Namely, if a machine is to be designed for a definite production per day, working on a scale forming solution, and if the cost figures, scale coefficients a and b are known, what is the optimum combination of heating surface area and time of cycle which will give the required production?

The solution of this problem might run like this:

Nomenclature:

U = Overall coefficient of heat transfer English units.
θ = Time since start of boiling, hrs.
θ_c = Time for cleaning and starting up per cycles, hrs.
θ_E = Time of evaporation, rhs. per cycle.
a, b = Constants in scale equation.
E = H_2O evaporation per 24 hr. day, lbs.
Δt = Working temperature drop, ° F.
A = Total heating surface of evaporator, sq. ft.
Q = Total heat transferred in evaporator up to time θ, B. t. u.
Q_c = Total heat transferred per cycle, B. t. u.
L = Heat input per lb. of water evaporated, B. t. u.
D = Days operation per year.
q = Fixed charges per year on evaporator, per cent.
s = Total cost, including auxiliaries, of evaporator, installed, dollars per sq. ft. heating surface.
S_1 = Labor cost during evaporation, dollars per hr.
S_2 = Labor cost during cleaning and starting up, dollars per hr.
C = Total cost per day, dollars.

$$\text{Basis} = 24 \text{ hr. day},$$

$$1/(U^2) = a\theta + b,$$

$$U = 1/\sqrt{a\theta + b},$$

$$(dQ)/(d\theta) = (U)(A)(\Delta t) = \frac{(A)(\Delta t)}{\sqrt{a\theta + b}}.$$

Integrating,

$$aQ_c = 2A\Delta t(\sqrt{a\theta_E + b} - \sqrt{b}).$$

The number of cycles per day is:

$$24/(\theta_E + \theta_c).$$

So the heat transferred per day is

$$\frac{24Q_c}{\theta_E + \theta_c} = \frac{48A\Delta t(\sqrt{a\theta_E + b} - \sqrt{b})}{a(\theta_E + \theta_c)}.$$

Solving for A:

$$A = \frac{EL(\theta_E + \theta_c)a}{48\Delta t(\sqrt{a\theta_E + b} - \sqrt{b})}. \tag{1}$$

So the fixed costs per day are

$$\frac{EL(\theta_E + \theta_c)(sqa)}{4800\Delta tD(\sqrt{a\theta_E + b} - \sqrt{b})} = \frac{e(\theta_E + \theta_c)}{\sqrt{a\theta_E + b} - \sqrt{b}},$$

where

$$e = \frac{ELasq}{4800\Delta tD}.$$

$$\text{The labor cost per day} = \frac{24}{\theta_E + \theta_c}(\theta_E\delta_1 + \theta_c\delta_2).$$

Since the steam cost per day depends only on E and L which are fixed, this cost will have no effect on the optimum.

The total cost, outside of steam is

$$C = \frac{e(\theta_E + \theta_c)}{\sqrt{a\theta_E + b} - \sqrt{b}} + \frac{24}{\theta_E + \theta_c}(\theta_E\delta_1 + \theta_c\delta_2).$$

C can now be evaluated for various values of θ_E and the optimum boiling cycle is easily found from formula (1).

Of course, the above method is of little practical utility because the values of a and b are not known for a machine that has not been built yet; but there may come a time when one can at least approximate them ahead of time. The problem you treat is much more practical at the present time, as it can be applied directly to existing machines.

DRYING RATE EFFICIENCY

Introducing a New Method of Efficiency Comparison in Drying Rates

By A. E. STACEY, Jr.

Research Engineer, Carrier Engineering Corp., Newark, N. J.

Read before Providence meeting, June 25, 1925

The rate of evaporation depends upon four factors.

1. The vapor pressure of the moisture in the material, corresponding to its temperature.

2. The vapor pressure of the moisture in the air, corresponding to its dew point temperature.

3. The effective velocity of the air over the surface of the material.

4. The physical and chemical properties of the material. The fourth factor is of importance in drying chemicals, as there might be an effect on the vapor pressure of the moisture in the material due to the presence of soluble salts or to some chemical change taking place during drying.

It is well known that the rate of evaporation of moisture, from different materials varies widely under the same atmospheric conditions. It was the purpose of the work covered in this paper to investigate the percentage drying rate curves of several chemical materials relative to the maximum drying rate.

Apparatus

The data were obtained from tests made in the laboratory of the Carrier Engineering Corporation. In each case a processing cabinet was used, so that, when desirable, the temperature, relative humidity and air movement were under control. Weight determinations were made without removing the material from the cabinet by extending one arm of the balance through the top. In this manner errors due to cooling and subsequent heating of the material were avoided. Precision grade thermometers, arranged so that the bulbs extended into the processing chamber through the holes in the top, were used in all tests. The air velocity over

the material was determined by an anemometer located in the same place as the material to be dried. Special pans, of several depths, were used for holding the material. These were arranged so as to be easily suspended on the balance.

Procedure

As there is usually a limiting temperature at which any material can be successfully dried without injurious physical or chemical changes, this, in most cases, determined the temperature to be used for a test. The temperature of the cabinet was raised to the desired point and the thermostat adjusted before the material to be dried was introduced. During the time of heating up the cabinet, the material was placed in the pans, loaded to the desired depth or weight, and weight determinations made. At this time small samples were prepared for bone dry moisture determinations in a Freas electric oven in the usual way. The temperature of this oven was maintained at 220° F. and the samples were held until no further loss of weight occurred.

As soon as the conditions in the cabinet reached the proper point, the material was introduced. Dry bulb and wet bulb readings were taken and at equal time intervals weight determinations made. The wet and dry bulb temperatures were recorded before the weights were taken to avoid errors due to the opening of the door in the side of the cabinet, and also from the stopping of the circulating fan which was necessary during the time of weighing.

From a series of readings taken as above, it was possible to plot curves using intervals of time as one ordinate and moisture loss as the other, thus obtaining a drying curve. However, for purposes of comparison it was found that curves plotted with one ordinate, based on percentage moisture removed or on residual moisture in the material, and the other ordinate percentage *rate* of moisture removal relative to the maximum rate of evaporation, i.e., the actual rate of the removal of water in pounds or grains at any instant compared on a percentage basis with the maximum weight removal attained during the drying, defined much more clearly the effect of changes on the rate of evaporation from the material. Moreover a rate curve of this type gives a graphical evaporative efficiency curve based on the maximum rate of evaporation from the particular material being investigated.

The rate curves were constructed from the drying curves in the following manner:

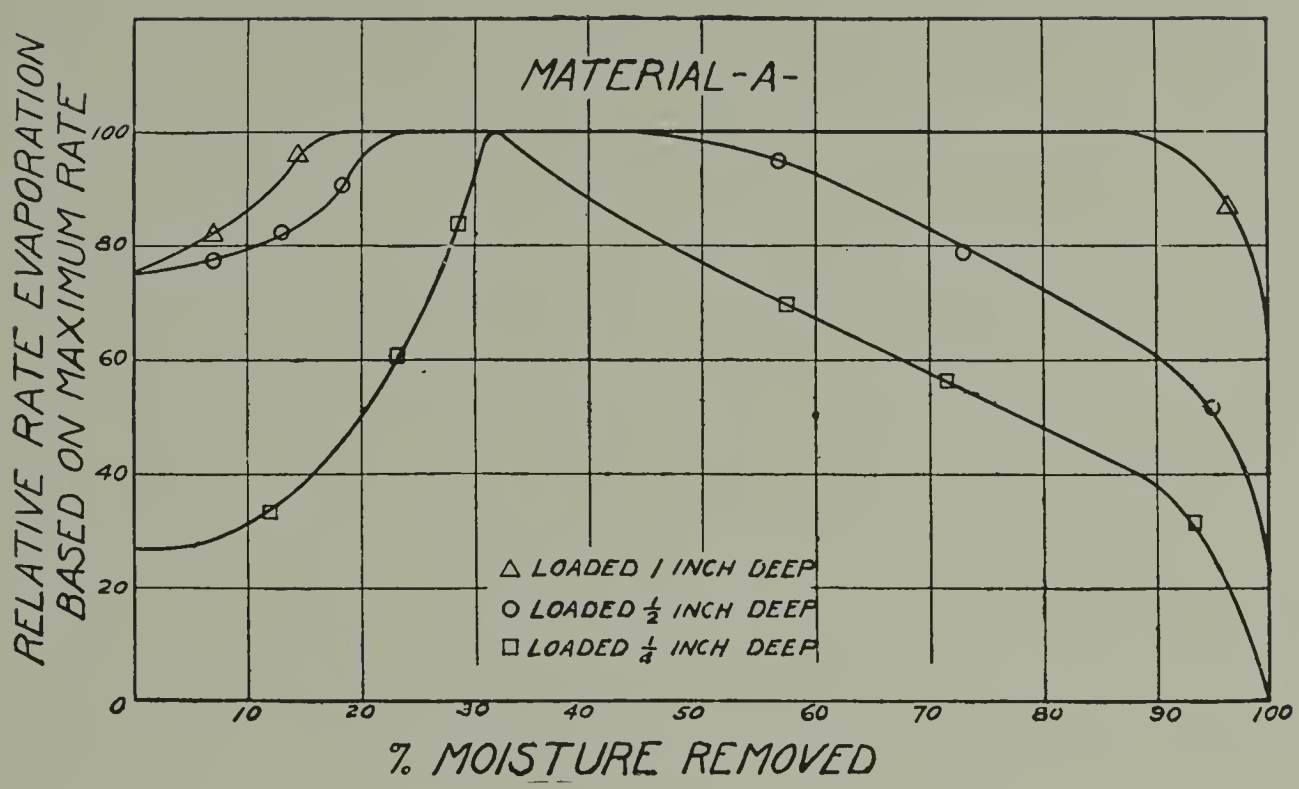

MATERIAL-A-
RELATIVE RATE EVAPORATION BASED ON MAXIMUM RATE
0
20
40
60
80
100
10
20
30
40
50
60
70
80
90
100
% MOISTURE REMOVED
△ LOADED 1 INCH DEEP
○ LOADED ½ INCH DEEP
□ LOADED ¼ INCH DEEP

FIG. 1.

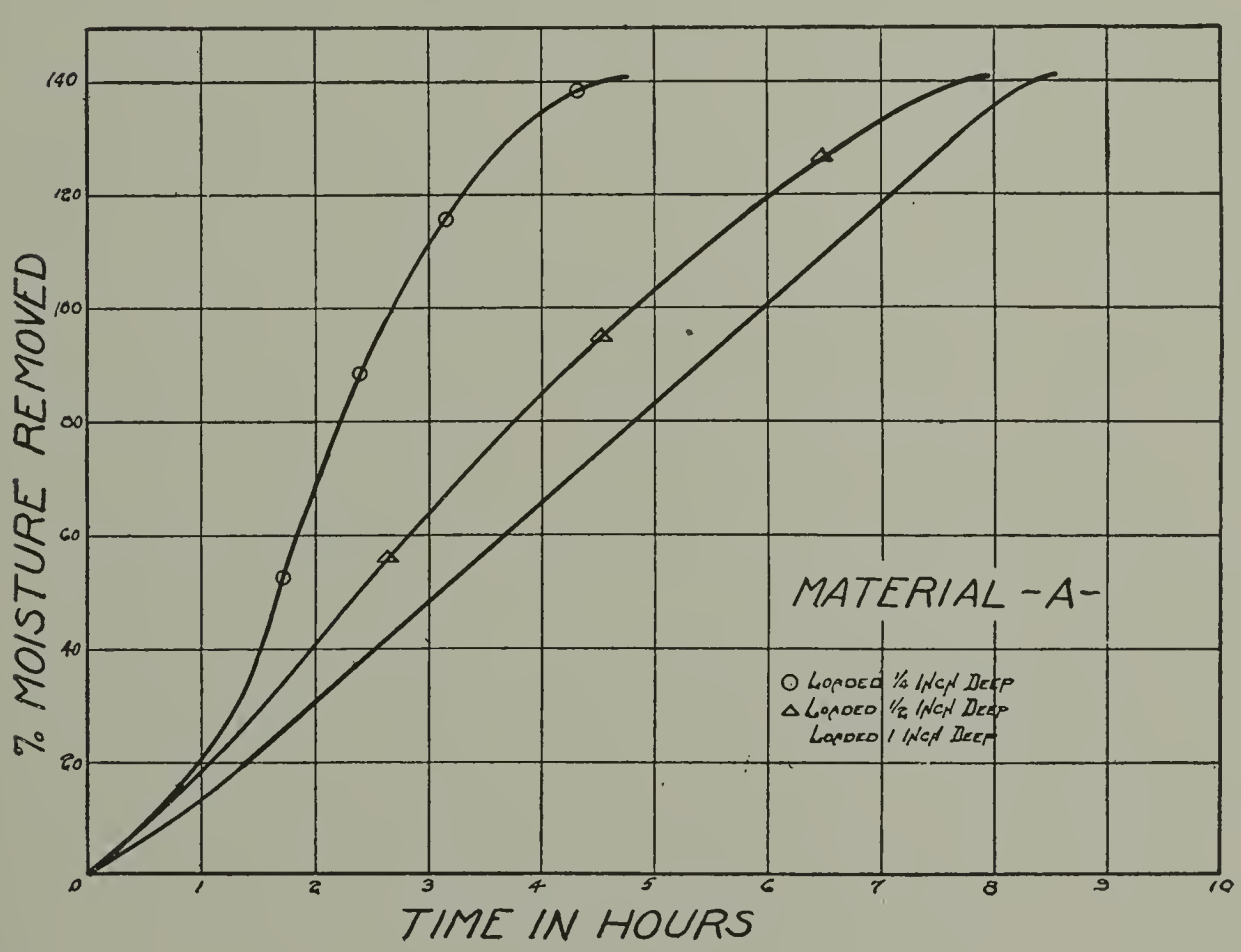

% MOISTURE REMOVED
0
20
40
60
80
100
120
140
1
2
3
4
5
6
7
8
9
10
TIME IN HOURS
MATERIAL -A-
○ LOADED ¼ INCH DEEP
△ LOADED ½ INCH DEEP
LOADED 1 INCH DEEP

FIG. 2.

Tangents were drawn to the drying curve at as many points as necessary, and the rate of evaporation at each point was determined. The total time of drying was then taken as 100 per cent removal of

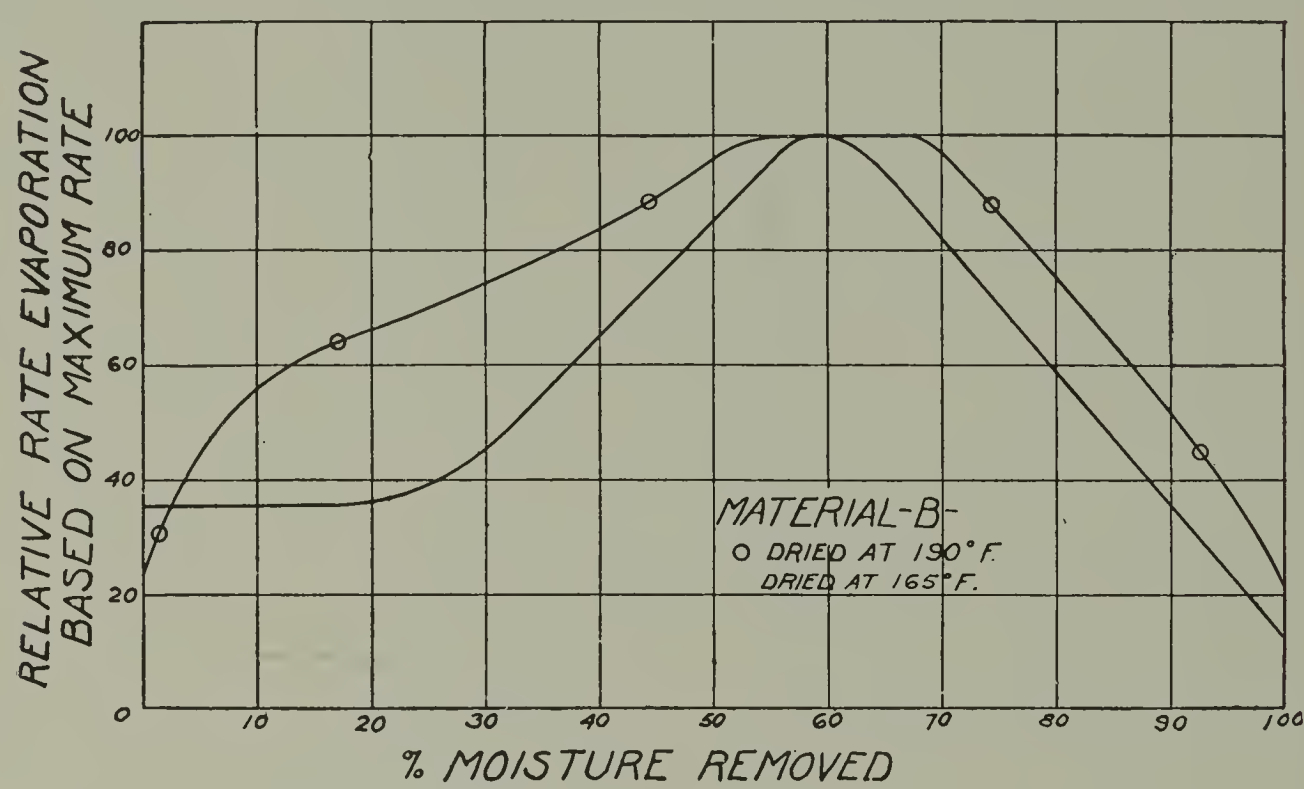


Fig. 3.

moisture from the material, and the relative rate of evaporation, as determined, plotted against the corresponding percentage of

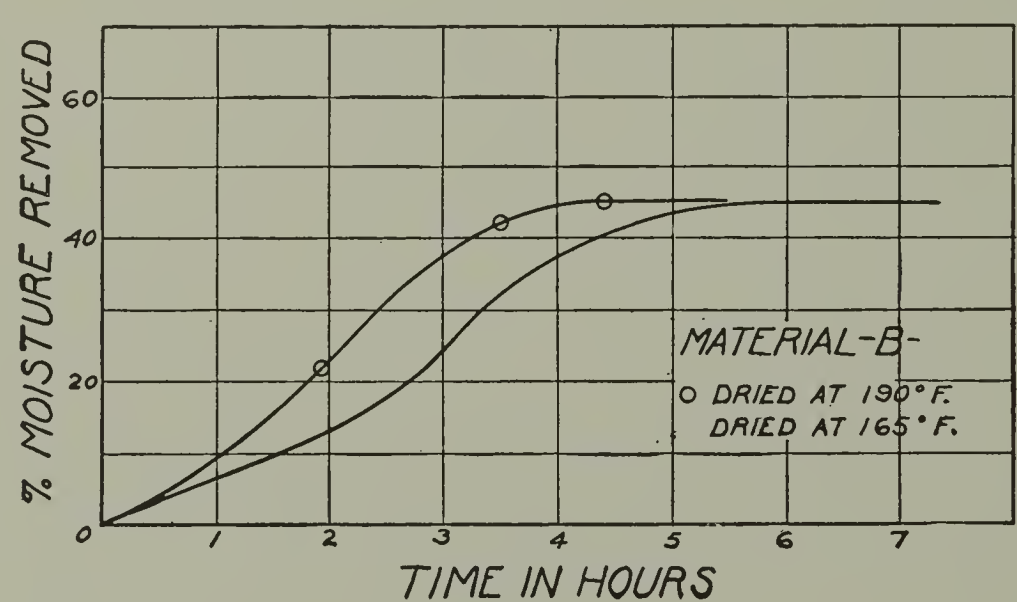


Fig. 4.

moisture removed from the material. This, then, gives a curve having as one ordinate percentage of moisture removed from material and the other relative rate of evaporation based on the maximum rate. It is evident, therefore, for maximum evaporative efficiency,

that the curve would form two sides of a rectangle, remaining at 100 per cent of the rate ordinate, until it reached the dry state at the 100 per cent moisture removed ordinate and then dropping

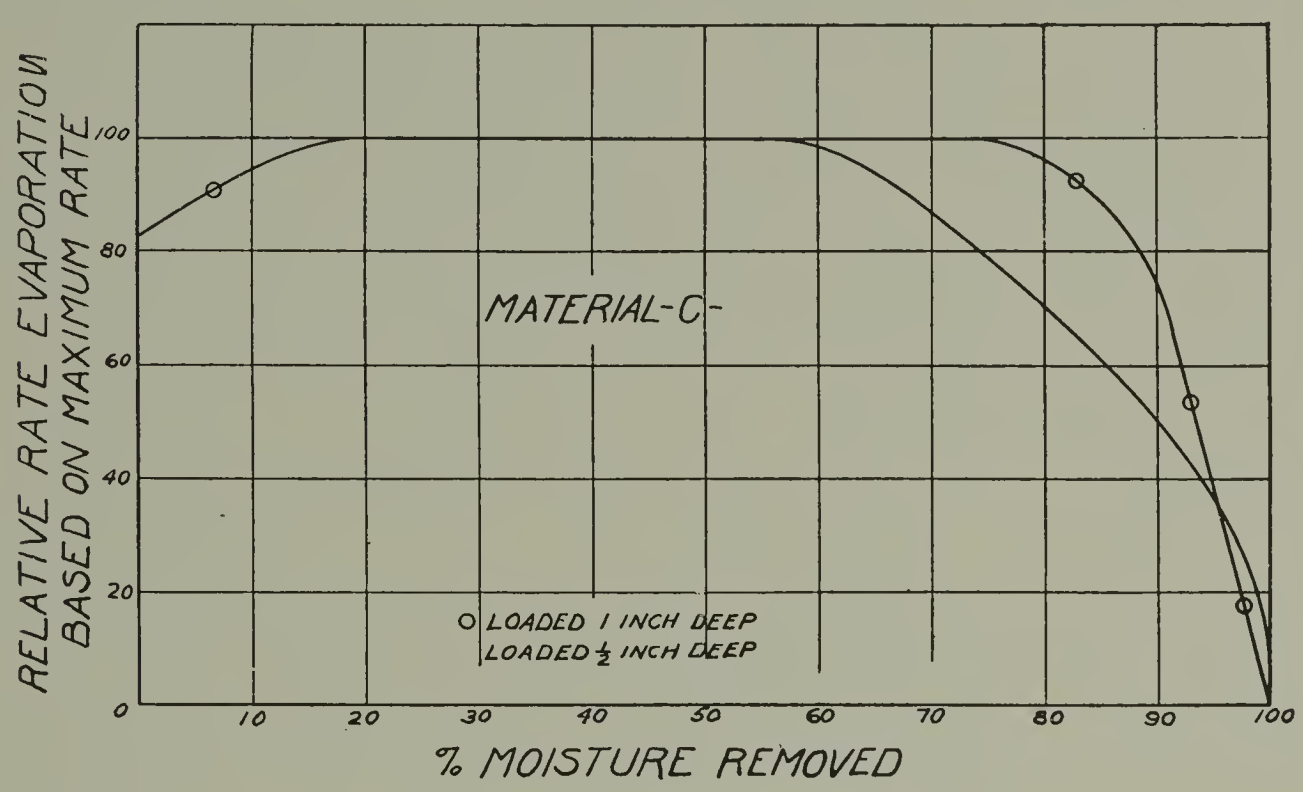


FIG. 5.

straight down to zero. If this area enclosed in such a rectangle were considered as 100 per cent drying efficiency, then the ratio of

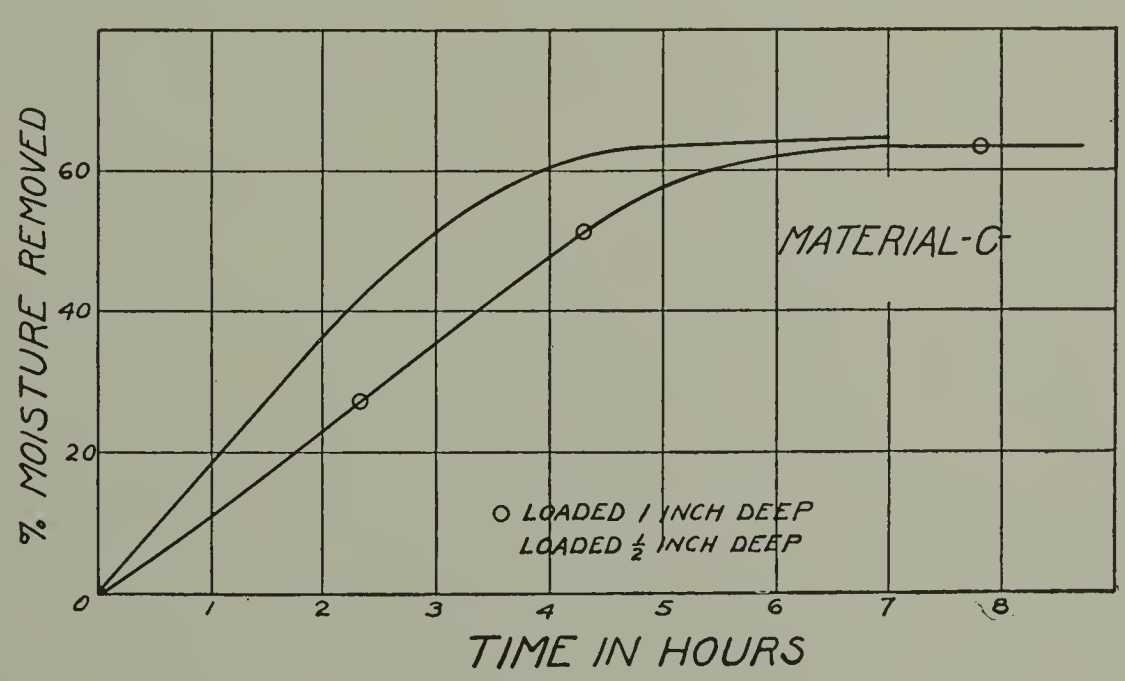


FIG. 6.

the area under any rate curve to the total area might be considered as the drying rate efficiency. It is on this basis that the following data are compared.

Material "A" (Figs. 1 and 2) was "Pulp Lead" containing 140 per cent moisture based on dry weight. It was about the con-

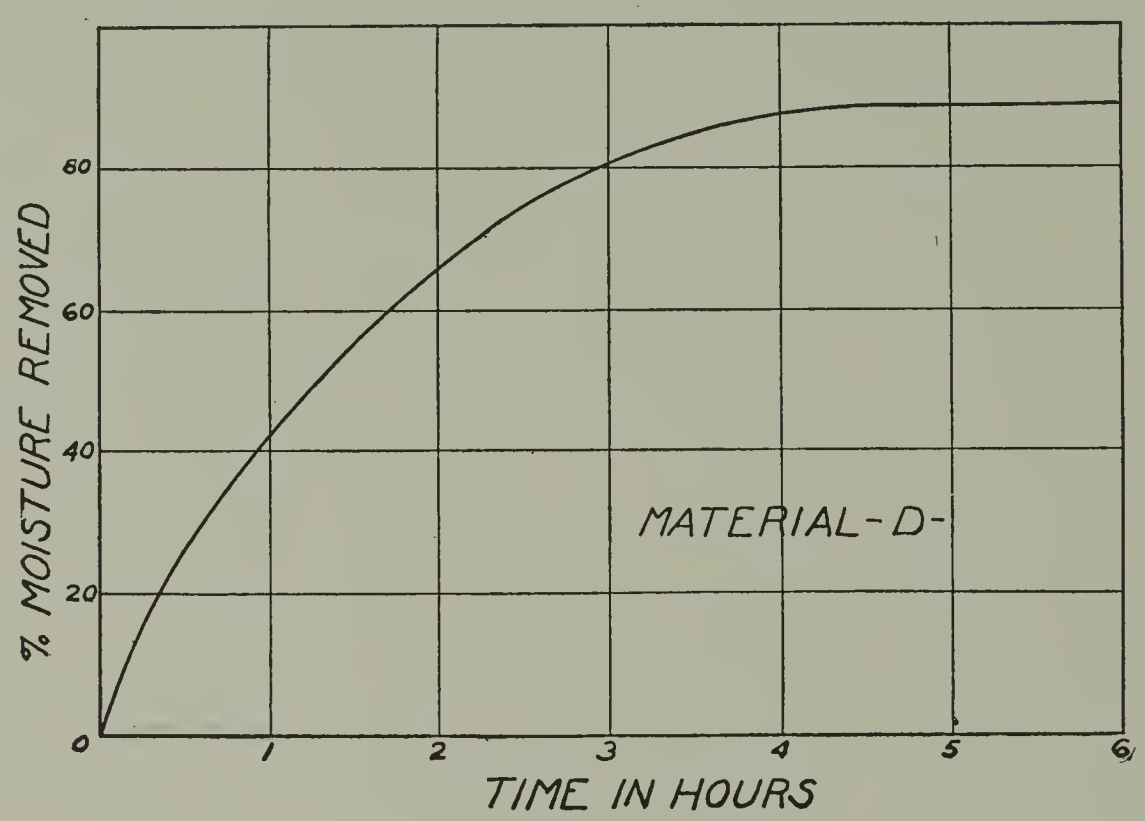


Fig. 7.

sistency of heavy cream. There was a tendency for the lead to precipitate leaving a liquid surface. This material was dried in

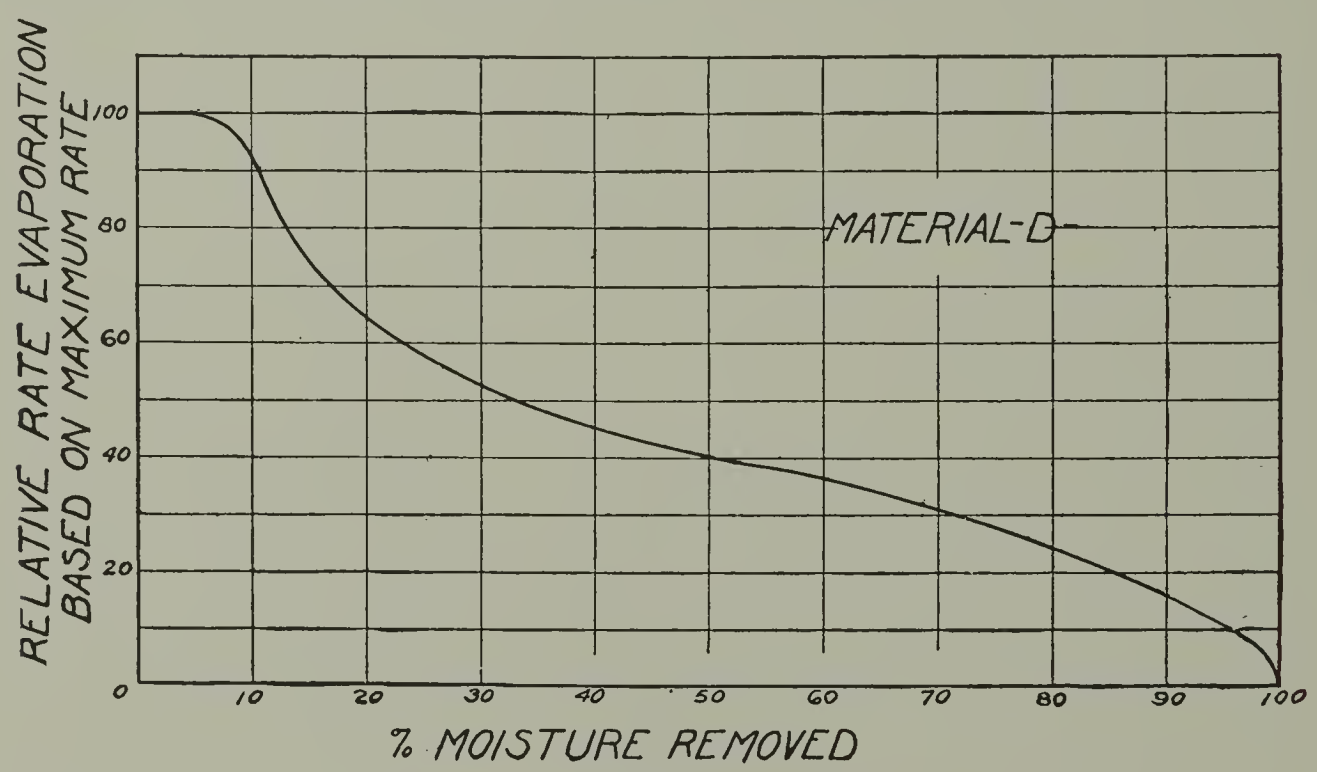


Fig. 8.

three depths ($\frac{1}{4}$ in., $\frac{1}{2}$ in. & 1 in.). From the drying curve, Fig. 2, it will be seen that the $\frac{1}{4}$ in. dried in $4\frac{1}{2}$ hours, the $\frac{1}{2}$ in. in $7\frac{3}{4}$ hours

and the 1 in. in $8\frac{3}{4}$ hours. This curve shows that a widely varying evaporative rate may be expected. On examination of Fig. 1, the rate curve, shows some interesting comparisons of the effect of

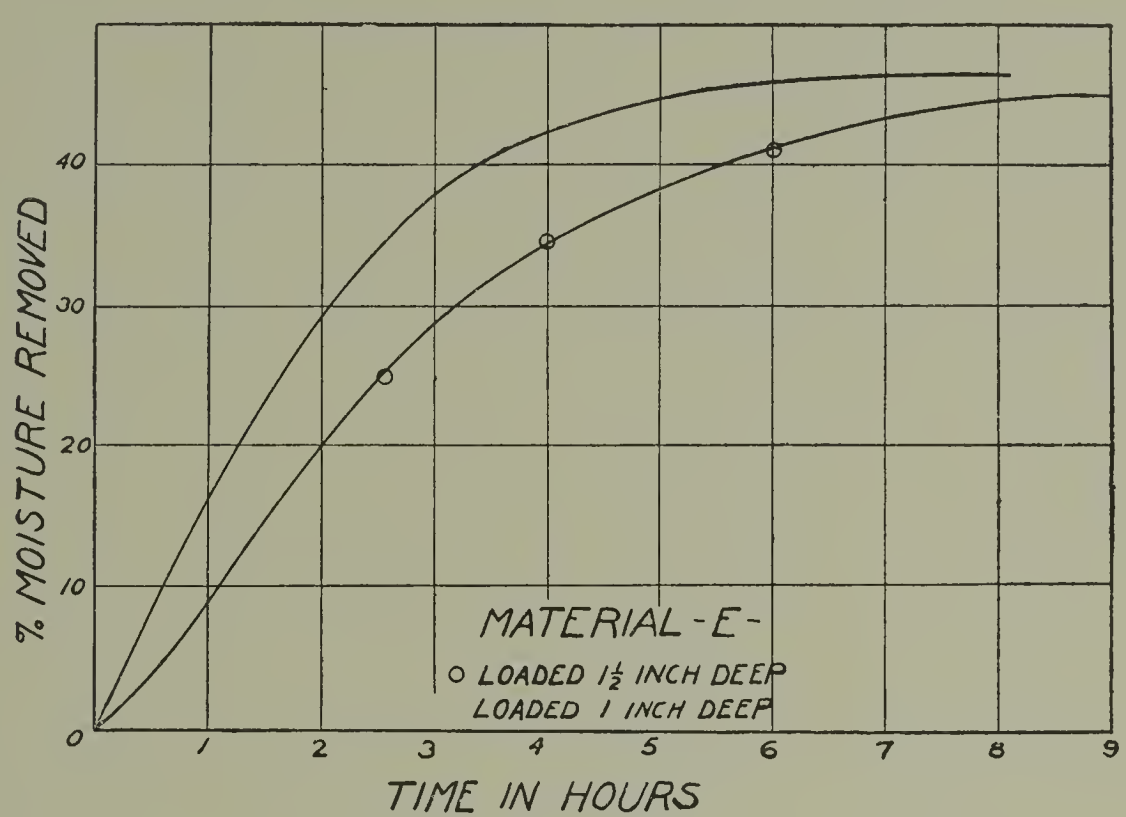


FIG. 9.

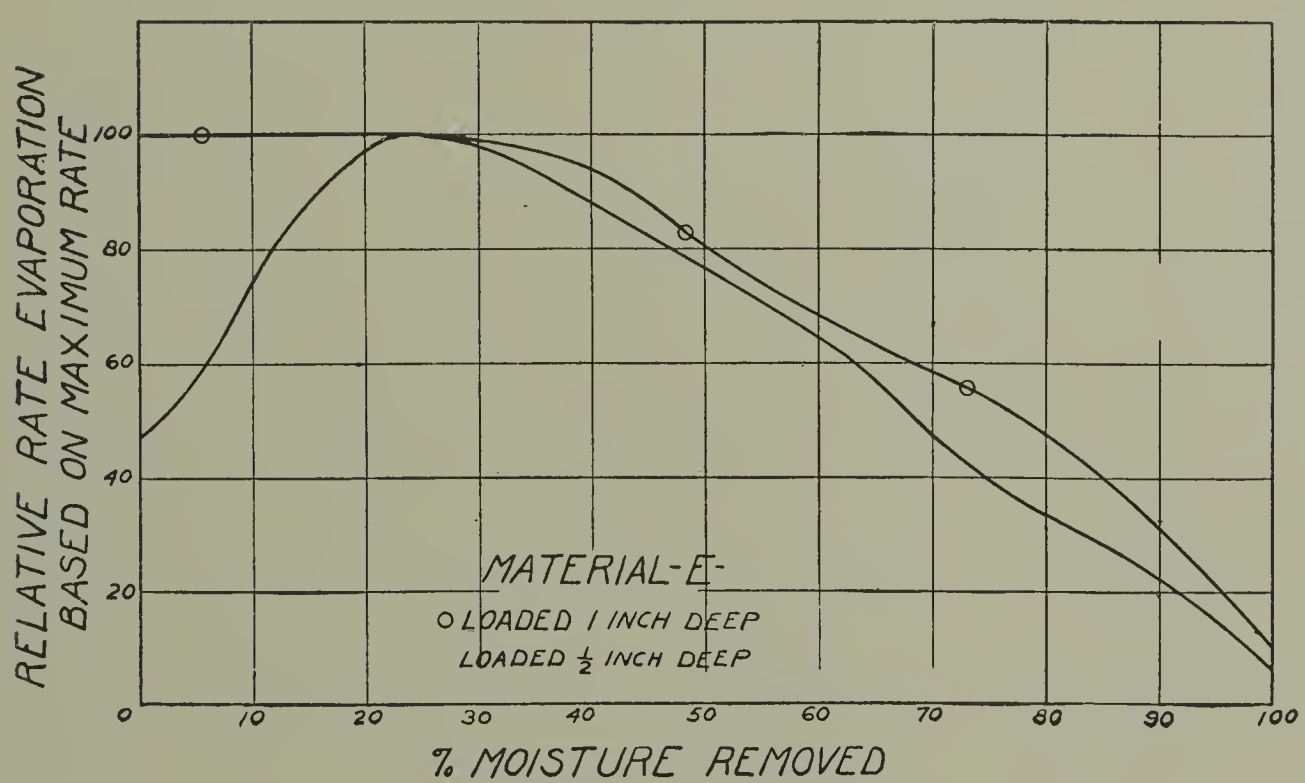


FIG. 10.

thickness of very moist material on rate efficiency. In this case, however, the big difference in efficiency of 57 per cent for $\frac{1}{4}$ in. to 96.2 per cent for 1 in. is not due so much to the thickness of drying

material, as to the separation of the pulp lead and water, thus leaving a free water surface exposed for a much greater proportion of the drying time. No doubt the slope of the latter part of the curve for the $\frac{1}{4}$ in. and $\frac{1}{2}$ in. indicates a tendency of the surface of the pulp lead to case harden and so retard the rate of diffusion of the moisture to the surface.

Material "B" (Figs. 3 and 4)—a color pigment. Pans loaded $\frac{1}{2}$ in. deep, moisture 83 per cent dry weight.

Material "A" gave a comparison of the rate efficiency as affected by the depth of loading while *Material "B"* is a comparison

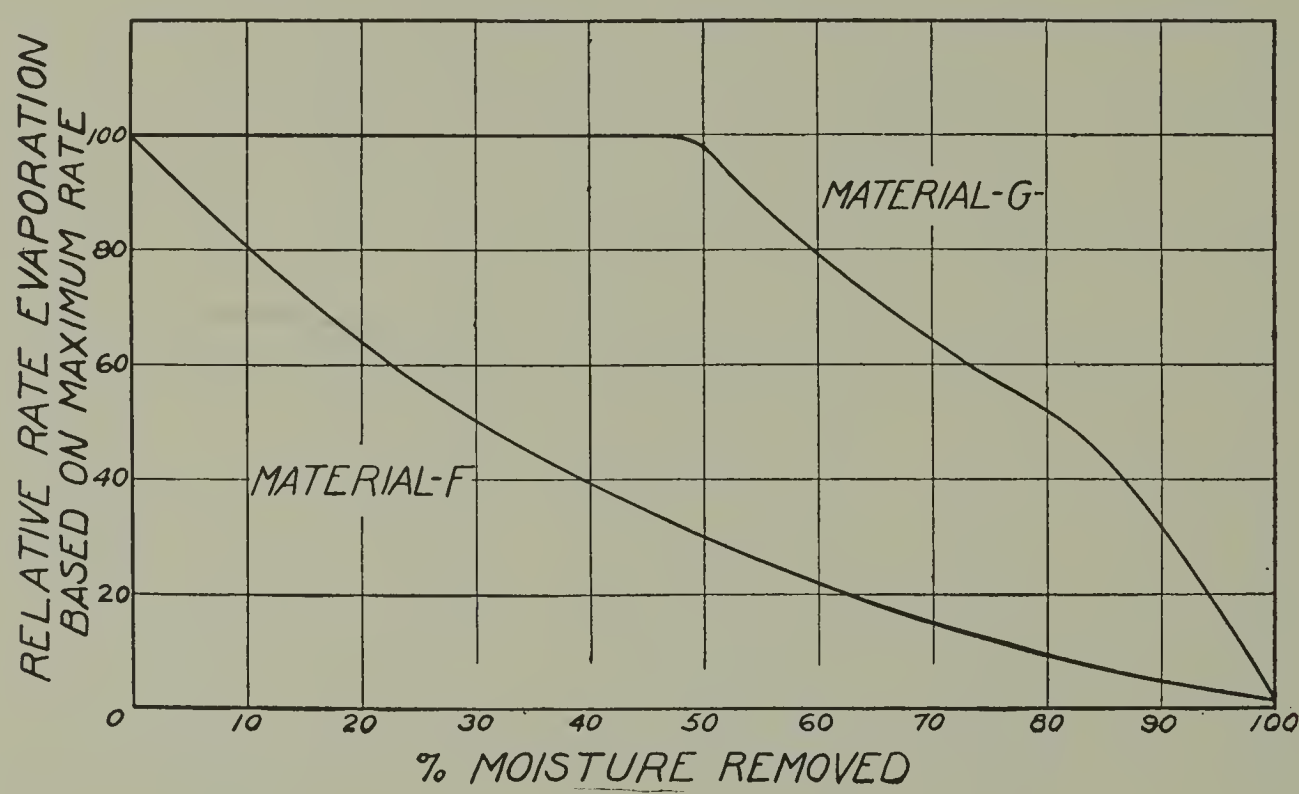


FIG. 11.

of the effect of temperature on the rate efficiency. In one case the material was dried at 165° F. giving a rate efficiency of $57\frac{1}{2}$ per cent. The material was then dried at 190° F. with a rate efficiency of 73 per cent. The diffusion rate in both cases was about the same, and the difference was in the time of heating the material through. The heat conductivity of this material is low. It is interesting to note, in connection with this test, that the maximum actual rate of evaporation was the same in both cases. This would indicate that the maximum rate of diffusion of the moisture through the material had been reached.

Material "C" (Figs. 5 and 6)—blue toner pulp. Moisture content 176 per cent dry weight, loaded $\frac{1}{2}$ in. and 1 in. deep. This is another material containing a large amount of moisture like

Material "A." The rate efficiency curves are characteristic in that they hold to the maximum rate throughout the greater part

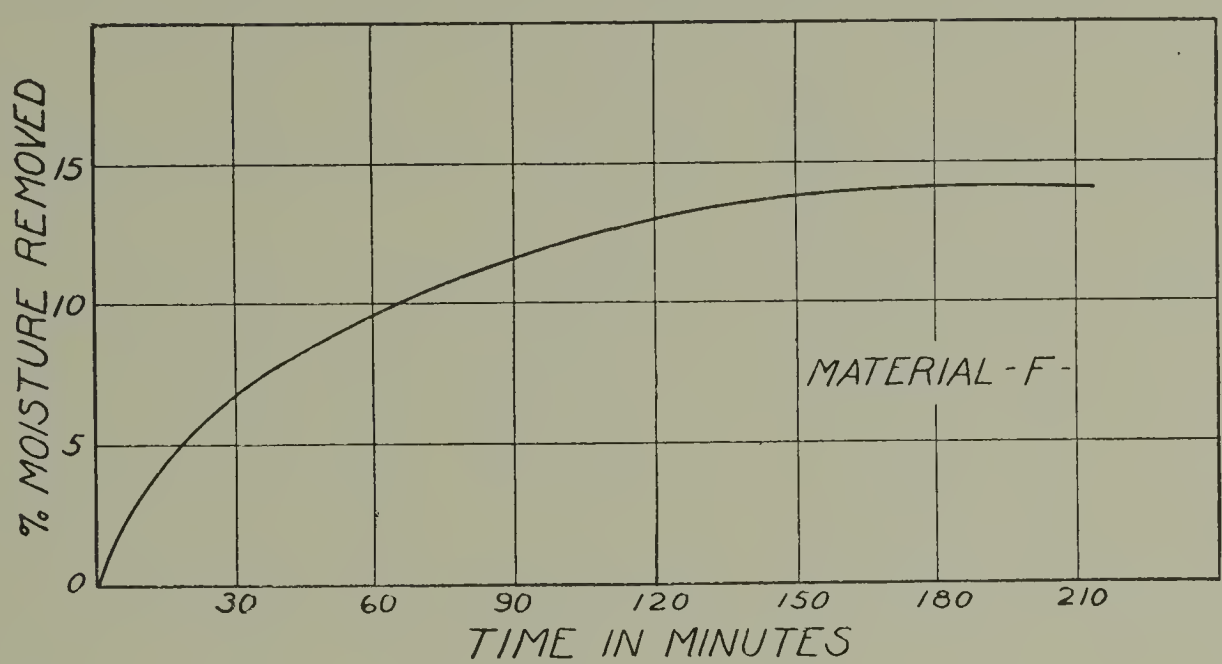


FIG. 12.

of the drying, thus a high rate efficiency is obtained; in the case of ½ in., 85.4 per cent and 1 in., 92.4 per cent.

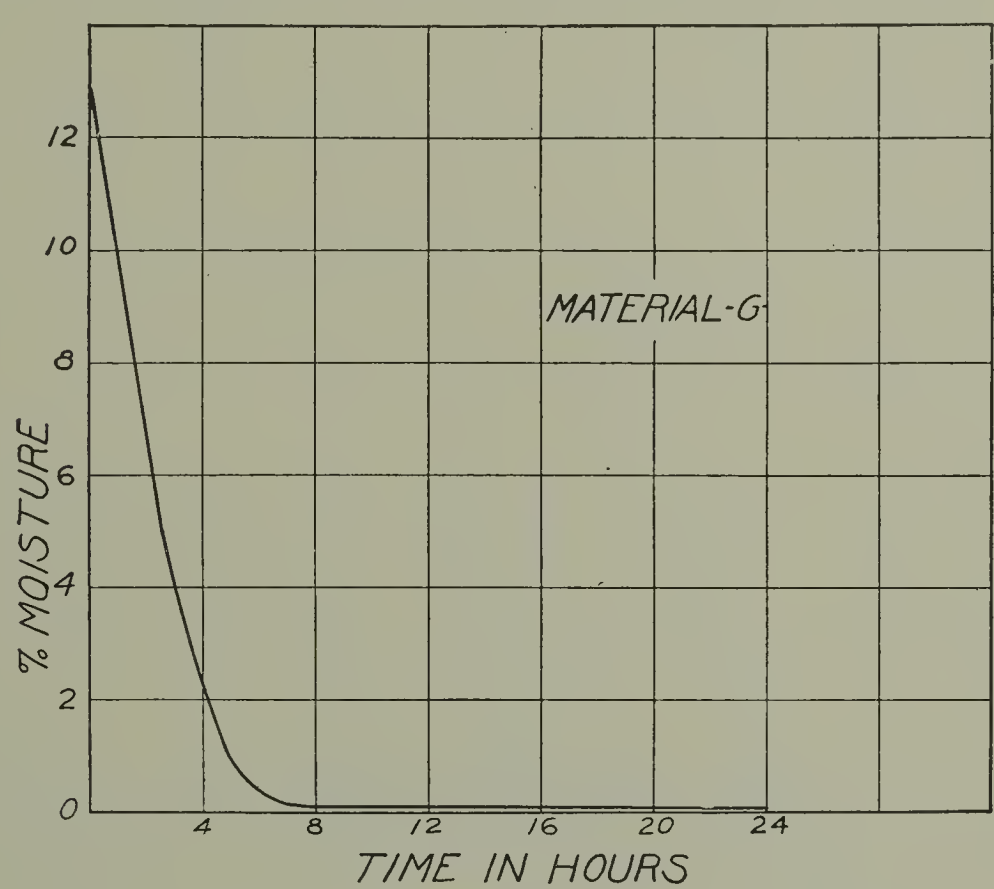


FIG. 13.

Material "D" (Figs. 7 and 8)—dye pigment. Moisture content 90 per cent dry weight, loaded 2 lbs. per sq. ft. The drying curve

for the material does not indicate the rapid falling off in the rate as shown by the rate curve. In this case the rate efficiency is 45.5 per cent or the average rate of evaporation is less than half the maximum. This would indicate that the material was being dried under the wrong conditions. In this case a higher relative humidity would no doubt have increased the rate of diffusion and shortened this time of drying.

Material "E" (Figs. 9 and 10)—copper carbonate, moisture content 81 per cent dry weight, loaded 1 in. and $1\frac{1}{2}$ in. deep. The moisture diffusion rate through this material was low in both cases,

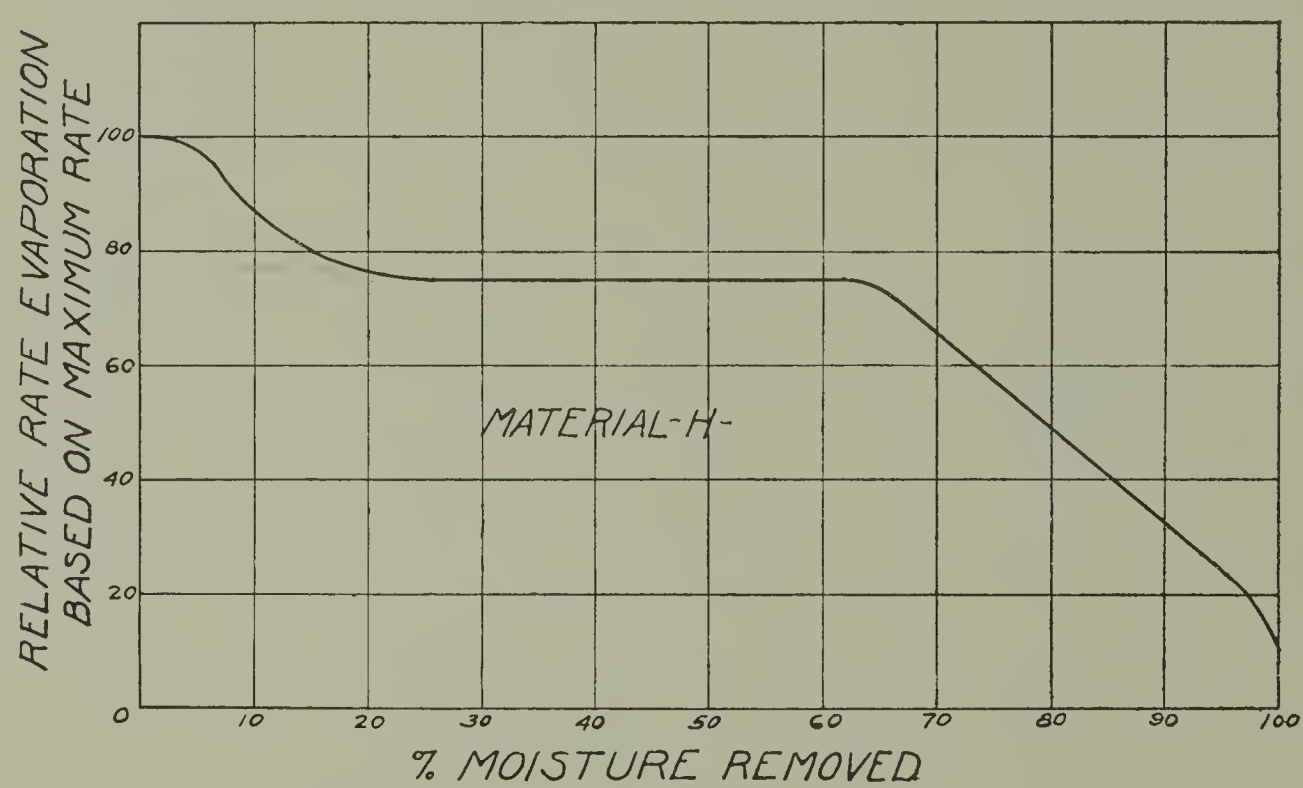


FIG. 14.

resulting in rate efficiencies of 63.3 per cent when loaded $1\frac{1}{2}$ in. deep and 92.5 per cent. when loaded 1 in. deep. This may be due either to a case hardening of the surface or to low heat conductivity of the material.

Material "F" (Figs. 11 and 12)—nitre cake fines. Moisture content 16.38 per cent, dry weight. This material was dried, removing all free moisture in three hours, at a temperature of 160° F. The rate curve gives the very low efficiency of 36.7 per cent, showing a gradual falling off from the start of the drying period. This material is unique in this respect.

Material "G" (Figs. 11 and 13)—barium nitrate crystals. Moisture content 13 per cent, loaded 1 in. deep. A very slow

drying material although the relative rate of moisture removal was 78 per cent. This is another case of moisture removal from crystals. The slow rate of drying, which seems associated with crystals, may be due to the increased space between the particles, thus reducing the capillary action, which is one of the means by which the moisture is carried from the interior of the material to the surface during drying.

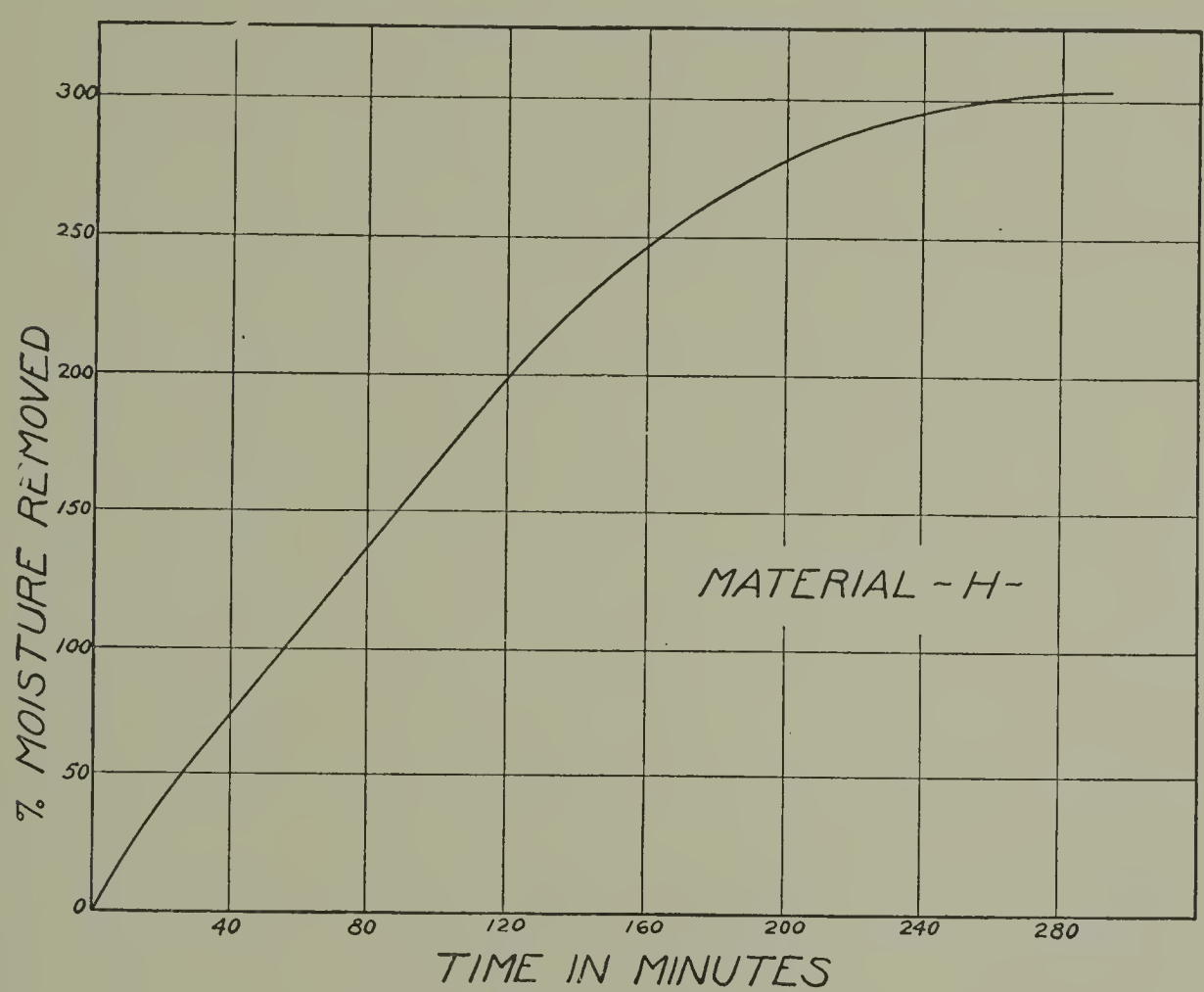


FIG. 15.

Material "II" (Figs. 14 and 15)—gelatine. Moisture content 313 per cent dry weight. This material is necessarily dried at a comparatively low temperature. The drying curve does not present any great difference from the curves of many materials. However, the rate efficiency curve is unusual in that the first part corresponds to evaporation from a free moisture surface, the second part shows a constant rate of diffusion and the final part a gradually diminishing rate of diffusion. The slope of the last section is exaggerated, due, no doubt, to a decreasing surface exposure.

Material "I" (Figs. 16 and 17)—white lead. Moisture content 42.5 per cent dry weight. The drying curve for this material shows

the long period of constant moisture loss and the heating up period. This is better shown by the rate efficiency curve. No doubt the

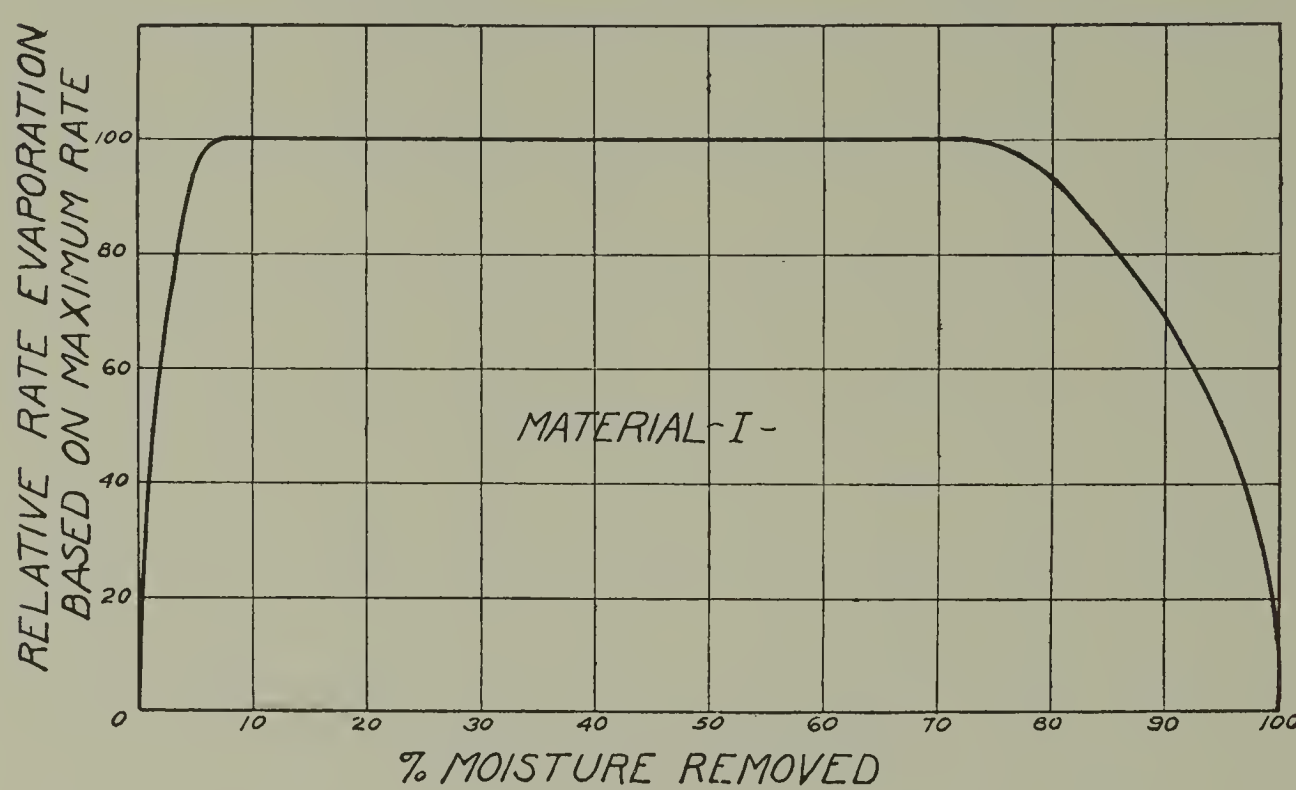


Fig. 16.

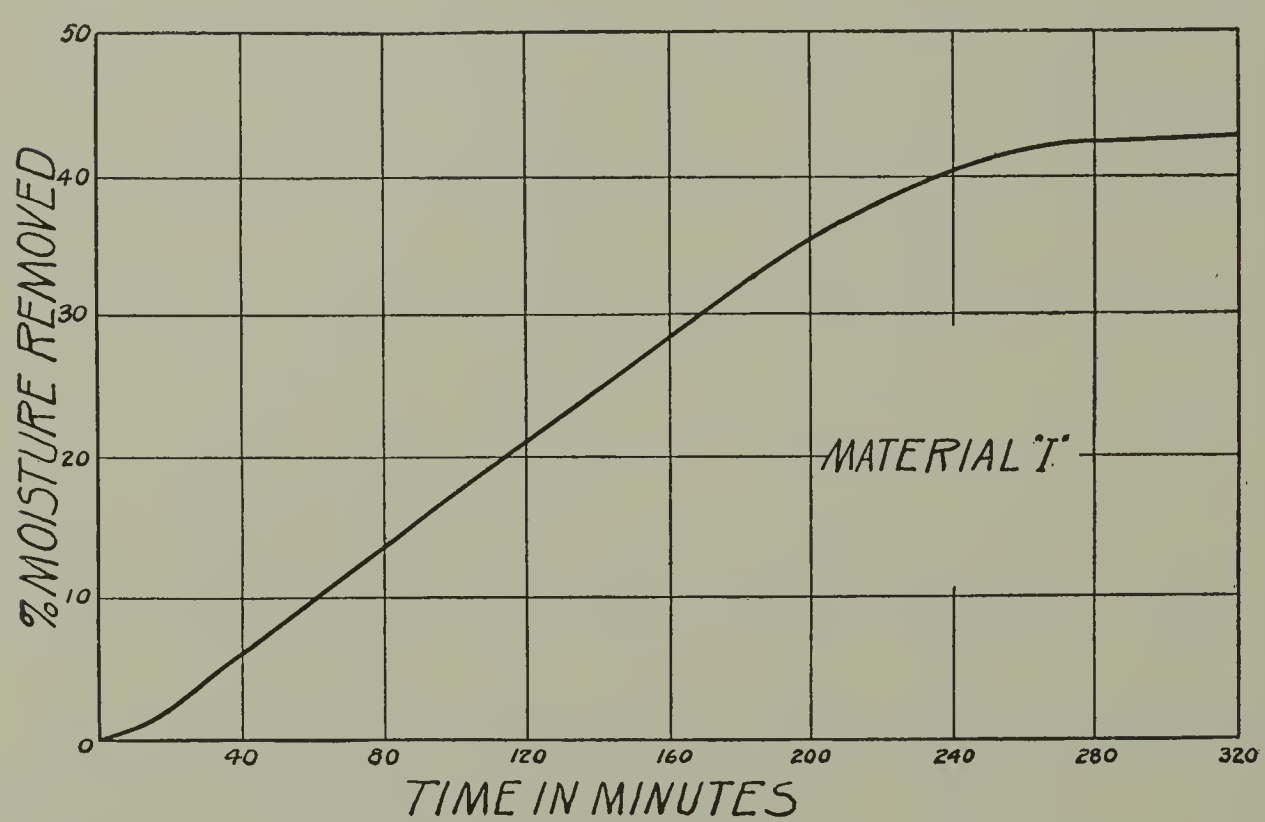


Fig. 17.

drying time could have been materially shortened in this case by increasing the temperature a little as no case hardening effect was shown in this experiment.

We have not in any of the above examples investigated the drying of hygroscopic materials such as starches, flours, etc. In cases of this kind it is usually desirable to remove moisture only to the point corresponding to the moisture regained under natural air conditions. This is usually considered at 65 per cent relative humidity and 80° F. When desirable this final moisture content can be regulated by control of the relative humidity in the final stages of the process.

THE USE OF EXPLOSIVES IN TRANSFORMER RESEARCH

By W. C. WILHARM and C. J. RODMAN

Read at the Pittsburgh Meeting, December 3, 1924

In recent transformer research it became necessary to study the cause and effect of arc and gas explosions that some times occur as a result of abnormal transformer operation. A new type of transformer was developed that would prevent a gas explosion and dampen the effect of the arc explosion as well as providing good assurance of preventing its occurrence. An explosion must be reproduced to study its effects, hence the problem suggests itself. This seemingly difficult problem was greatly simplified by the use of artificial explosives. Definite chemical composition of explosives, ignited under similar conditions gives comparable amounts of gas and pressure. The generation of pressures by such materials gave the desired results as was verified by the many tests made.

Although a large transformer must be strong enough to withstand excessive pressures due to any contingent abnormal duty it must, nevertheless be made of rigid construction. The mass of copper and iron, that makes up the working parts of a transformer, and which is submerged in upwards to 9,000 gallons of oil exerts a pressure on the large steel tank. A strain is also exerted on the tank when the whole equipment is transported from place to place suspended from a crane. The structure and material composing the tank, which is boiler plate steel, is made rigid enough to withstand these service strains, but when excessive powerful pressures are suddenly applied protective equipment must take care of them. Various types of relief devices for controlled release of sudden expansions have been developed. One of the purposes of the explosion tests was to assist in final decisions as to their value.

It is not the purpose of this paper to go into a discussion of the cause of transformer breakdowns; it being sufficient to state that they do break down or rupture from various causes.[1] An arc forms

[1] "Arc Action on Some Liquid Insulating Compounds," Rodman, *A.E.S.*, Sept. 25, 1922.

"Causes and Prevention of Explosions in Power Transformers," O. H. Eochholz, *Elect. World*, June 24, 1922.

which is intensely hot that breaks down or cracks the oil. The resulting products of arc decomposition of the oil are carbon, some hydrocarbons of lower molecular weight, and highly combustible gases such as hydrogen, methane, and unsaturated hydrocarbon gases. These gases when mixed with air exist as a potential serious explosion hazard.

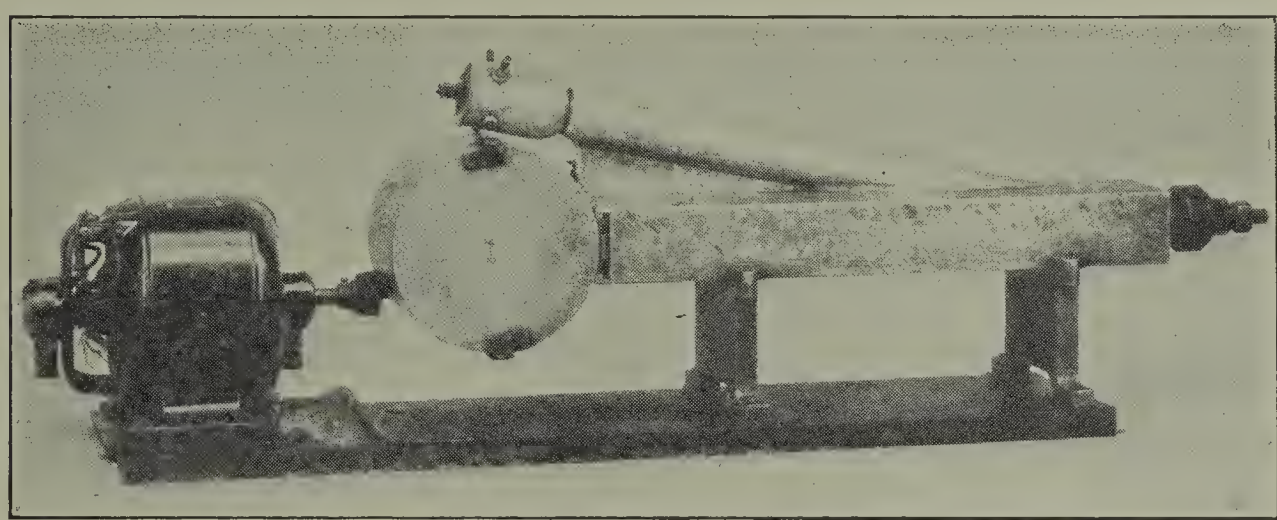
The change from the liquid oil to a gas under the heat of the arc causes an expansion of explosive violence and it is this effect of energy that is called a primary explosion. These gases rise to the top of the oil, and when mixed with oxygen or air present and subsequently ignited, a secondary or gas explosion of more or less violence occurs.

It was in the research for the prevention of such transformer failures that explosives were requisitioned for a rôle entirely unique from their usual application. It was desirable to duplicate the sudden pressures due to arc energies and the more violent secondary explosions in terms of engineering precision.

A preliminary study of the relation of arc energies to the energy produced by artificial explosives such as gunpowder and dynamite was made in a small steel tank 16 inches in diameter and 28 inches high. Various devices for measuring and recording the pressures were tried. A small gauge consisting of a piston that forced a hardened steel ball into a lead disc gave fairly good results for maximum pressures. The measurement of the diameter of the cavity left by the ball gave an indication of the pressure of the explosion. Another type was the one used by the U. S. Navy consisting of a series of holes in a block ranging from 1/16 of an inch to 1 inch in diameter, covered with a sheet of standardized paper. The degree of pressure was estimated from the diameter of the smallest hole that had its paper cover punctured. This did not prove satisfactory, as the paper although impregnated with supposedly water and oil proof material would not stand up when immersed in oil.

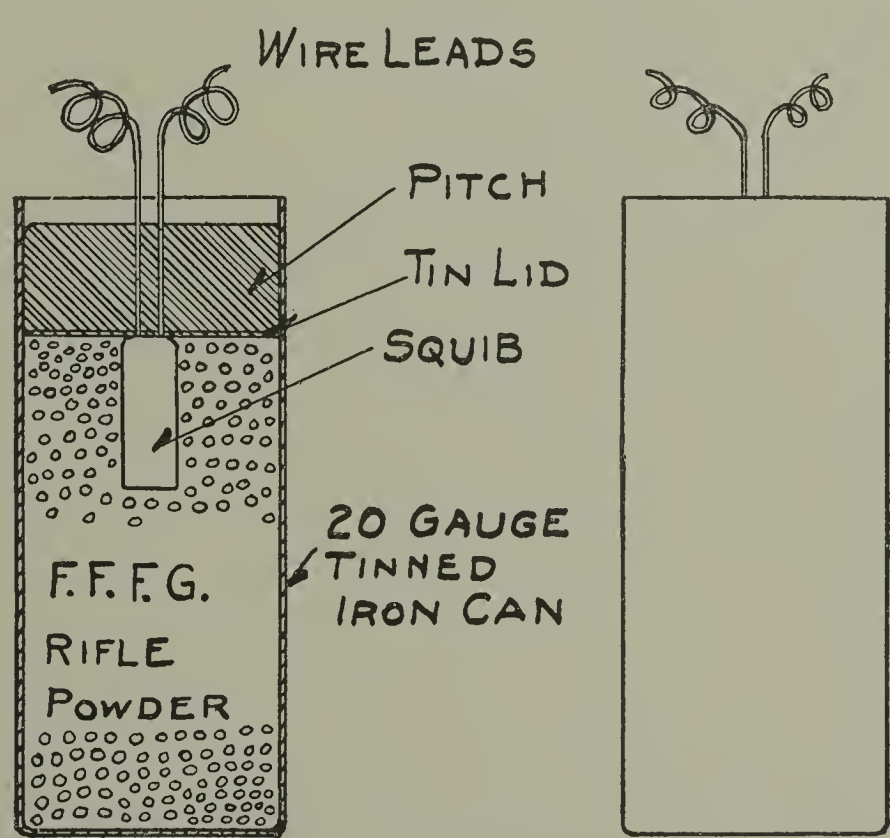
The gauge problem was finally and satisfactorily solved through the courtesy of the U. S. Bureau of Mines. Several instruments developed and used by the engineers of the Bureau for Mine Explosion Work were obtained. This type of instrument, the result of years of development in the measurement of pressure recording devices has a hardened steel disk, one face of which is exposed to the pressure or explosion. Deflections of this disk are transmitted

by a small pin point to a pivoted mirror, which reflects a beam of light from a fixed point source to a strip of sensitized film on a revolving drum. Instantaneous pressures exerted on the steel disk are



Recording Pressure Gauge

reproduced by the line traced along the rotating film, thus giving a graphic record. A time scale is simultaneously recorded from a 60-cycle light beam directed upon the margin of the film. By

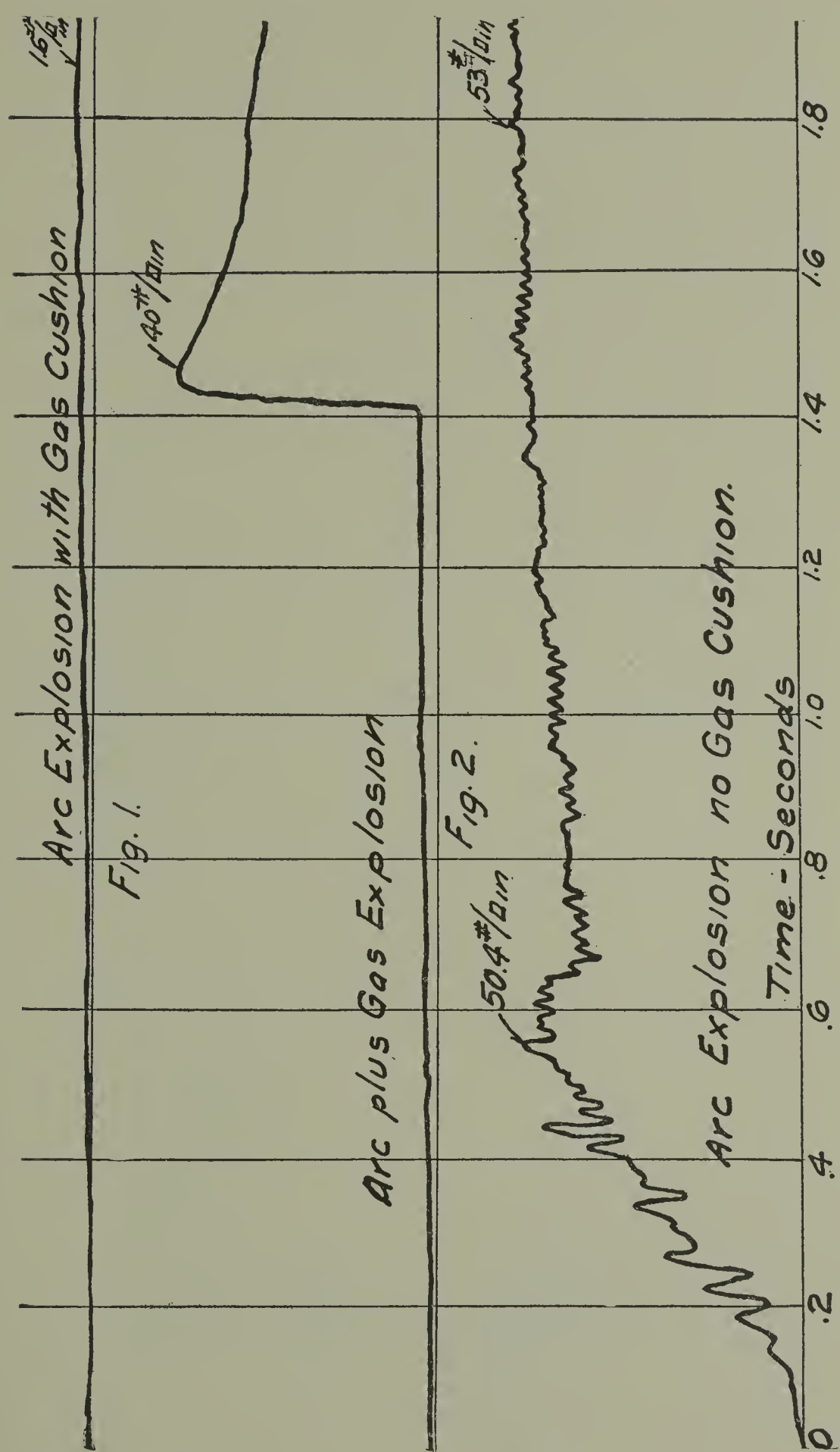


Explosion Test Bombs

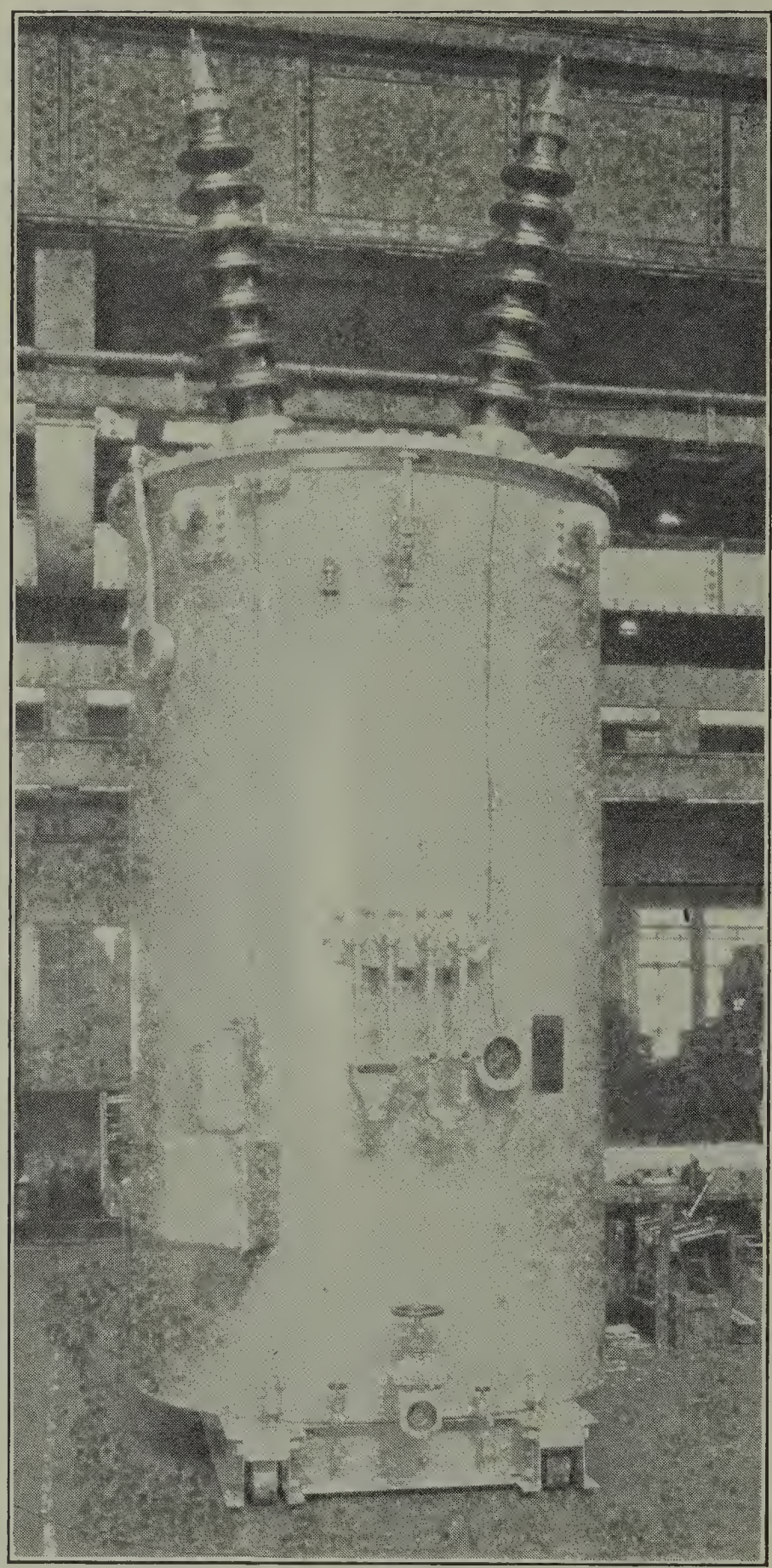
comparing the results of electric arcs and secondary explosions with those produced by various artificial explosives a very close analogy was found.

After some experimental work with numerous powders and chemicals and also numerous bomb constructions as well as with means of firing, a standard unit of rifle powder was selected for the experiments. The bomb as finally constructed, consisted of a can made of 20 gauge tin plated sheet iron $1\frac{1}{4}$ inches in diameter by 3 inches long filled with 40 grams of Du Pont F.F.F.G. rifle powder. A Du Pont electric squib was imbedded in the powder and a lid made of the same material as the can, punched out to the exact inside diameter of the can, and with a 1/8 inch hole in the center for the lead wires, was pressed into place. The pressure used in pressing on the lids was made constant for every bomb. The lid was then sealed in with a layer of pitch, making it water and oil proof, and then the top edge of the can was crimped in on the pitch. This made a uniform unit that gave very good results. The pressure was increased by adding the desired number of bombs and wiring them to the current supply in parallel. They were wired in this manner so the firing would be simultaneous, with no lag between the various units of the charge.

In a small tank (the same as referred to above) arcs were created between electrodes submerged in the oil. The tank was filled with oil to within 4 inches of the top and the cover bolted on. The space between the oil and the cover was filled with nitrogen gas and then the arc was created. In this test and duplicate tests a pressure of 1.6 pounds per square inch was created as is shown on the graph in Fig. 1. This gave the effect of an inert gas cushion using electrical discharge. For the effect of an air cushion the 4-inch gas space was filled with air, containing, of course, approximately 21 per cent oxygen. The arc was then created and was soon followed by an explosion of the gases that had risen from the arc action on the oil when mixed with the air of the gas cushion. This is plainly shown on the graph in Fig. 2, by the precipitous climb to 43 lbs. per square inch pressure. The gas cushion was then eliminated and the tank filled entirely with oil. This condition represents another type of transformer. When the arc was created as before, there was no secondary explosion, there being no oxygen present, but the pressure from the arc energy exceeded that of the gas or secondary explosion as is shown on the graph in Fig. 3. The above preliminary tests give data which show a direct relationship between explosions caused by arc struck beneath the oil, a secondary explosion and a gun powder explosion.



Pressure Grams of Small Scale Arc and Gas Explosions



The Inertaire Transformer

When an electric arc is discharged beneath the surface of similar oils the amount of gas released has a definite ratio to arc energy expended. The amount of gas for transformer oil is about 97 cubic centimeters per kilowatt second of arc energy expended. Therefore the quantity of gas and the pressures built up can be predicted if

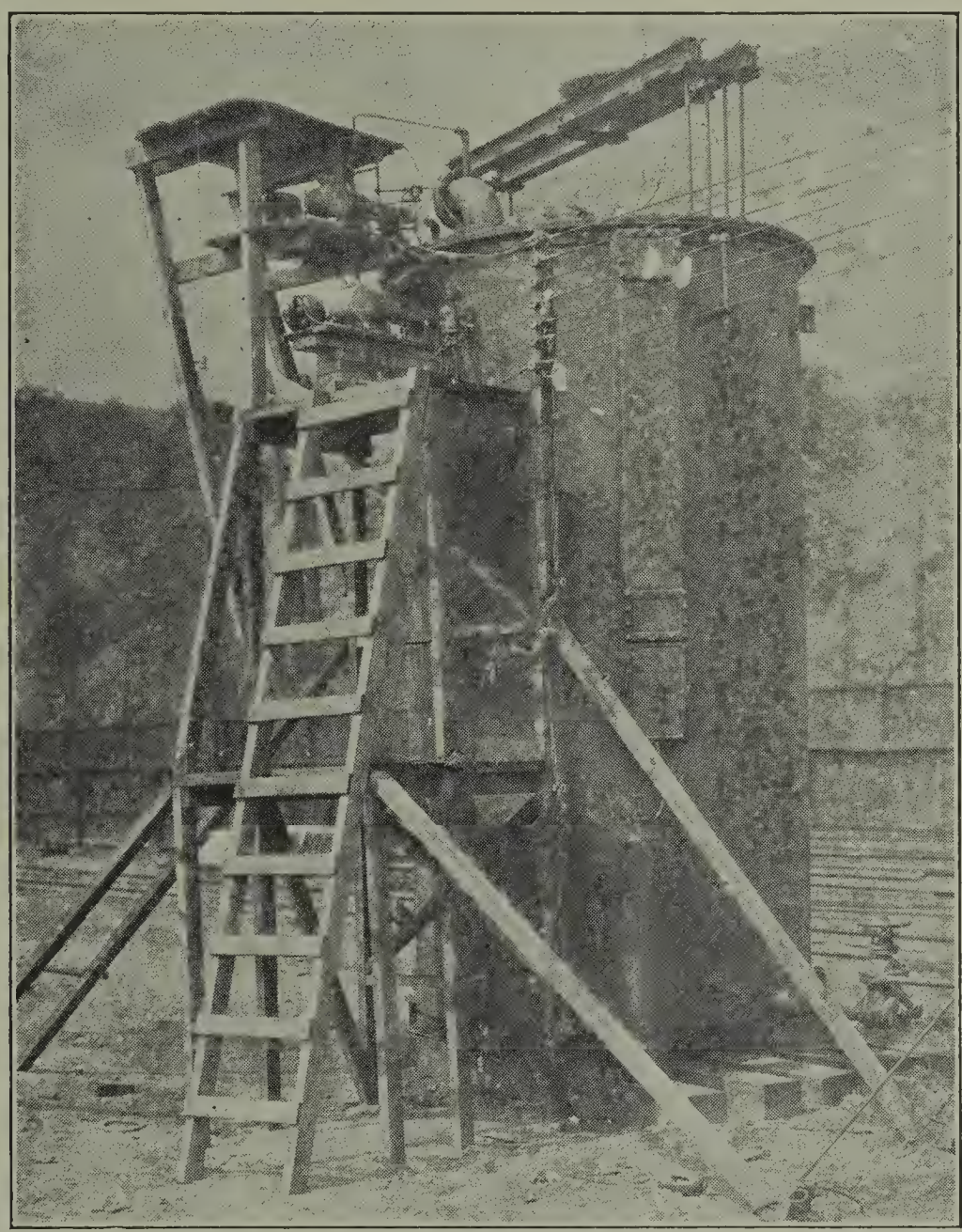
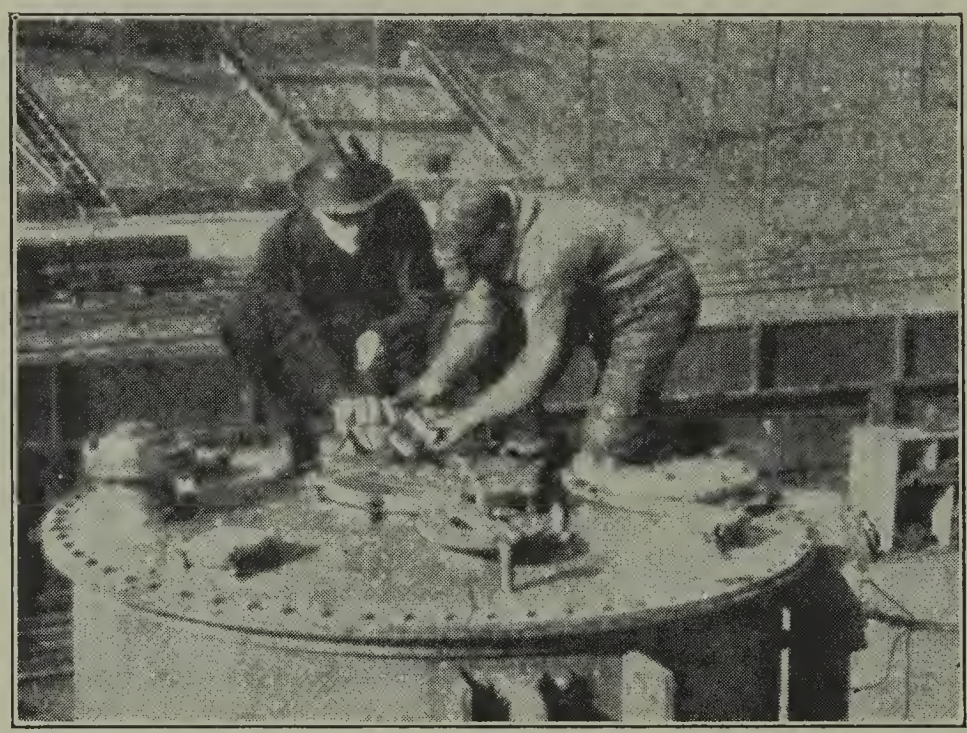


FIG. 4. Large Transformer in which Explosion Tests were made, showing also Pressure Gauges and Some Inertaire Apparatus

the arc energy is known. On the other hand, the quantity of gas evolution produced from powder fired under controlled conditions, is also known. Hence a comparison of pressures due to release of gas by powder or arc is made. These pressures were measured experimentally and the effects recorded on the graphic charts. It is interesting to note the similarity of curve form of powder ex-

plosions and those produced by secondary explosions of arced oil combustible gases in air.

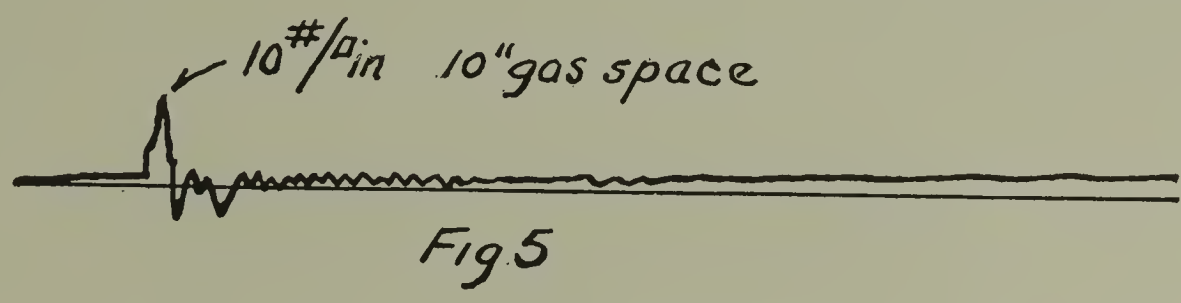
The amount of gas evolved from rifle powder varies slightly with various densities of loading. The mean volume evolved from one gram is 259 cubic centimeters which would be equivalent to 2.67 kilowatt seconds of arc energy. The ratio of 1 gram of powder to 2.67 kilowatt seconds of arc energy, gives equal volumes of gas at normal temperature and pressure. The volume of gas from one bomb is about 10.3 liters or .36 cu. ft. The high temperature of either the rifle powder combustion or of the electric arc greatly enhances the volumes of gas instantaneously liberated.

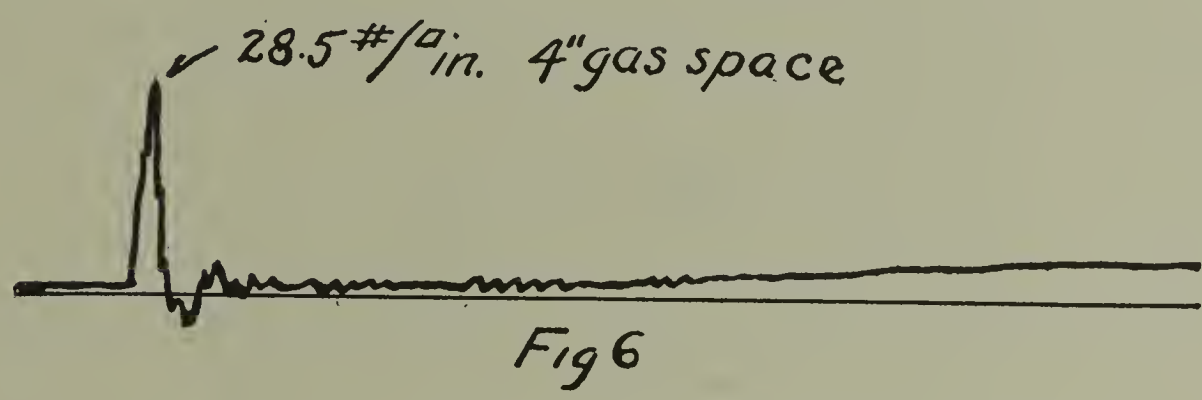


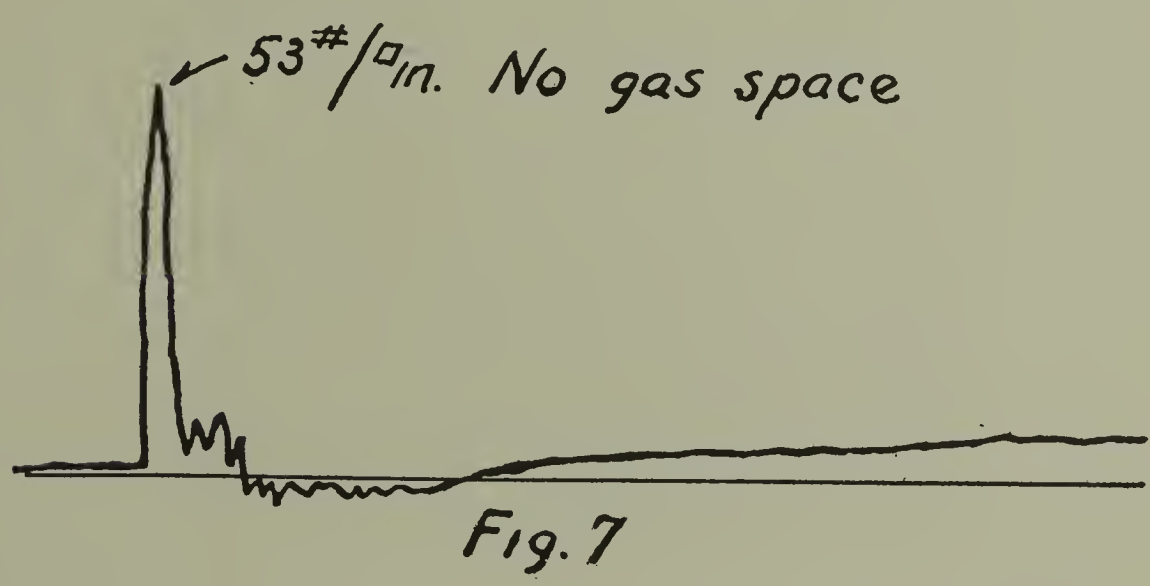
Bombs Before Lowering Into Tank

Knowing the power of the rifle powder bombs, in cubic feet of gas liberated and pressure obtainable and the pressure equivalent of arc energy everything was ready for the practical tests on a large size transformer. A set-up as shown in Fig. 4 was constructed. It consisted of a transformer of the 66,000-volt type measuring 72 inches in diameter by 134 inches high. The boiler plate cover differed from the general type in that it contained a new type of pressure relief device (see Fig. 5) which is gas tight until ruptured by an explosion. After the rupturing of the diaphragm the excess pressure is released and the lid is drawn back by springs to a well fitted seat. This excludes the outside air that would diffuse into the gas space if there were an open hole. The bomb

firing and pressure indicators were controlled automatically in their proper sequence. When the stage was all set up for the explosion, a single switch started the film drums rotating, lighted the timing lamps and fired the bombs. The gas cushions (the







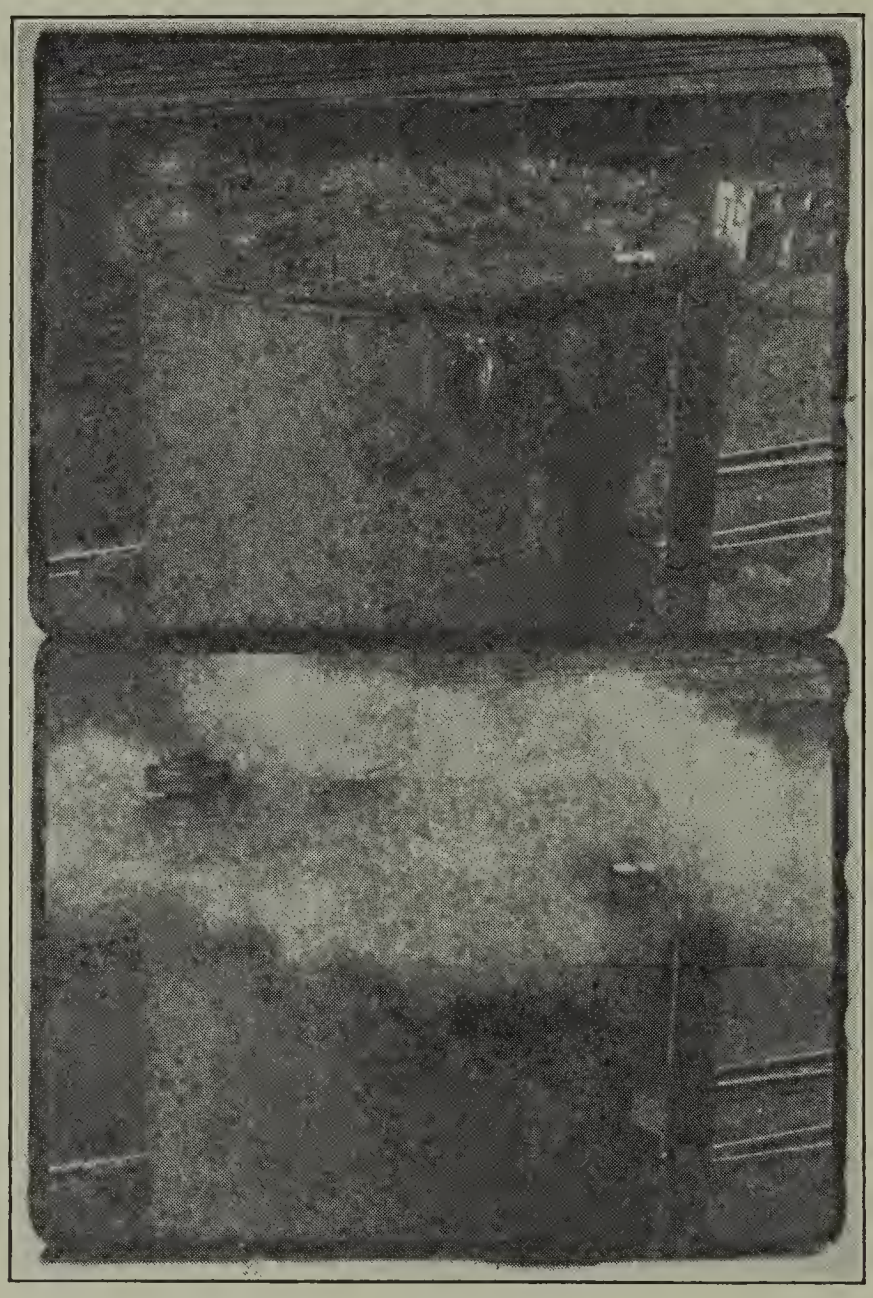
Pressuregrams of Large Scale Explosions Using 120 Grams Each of Powder

space between the oil level and the cover) ranged in depth from 12 inches to zero. The charges consisted of 3–40 gram bombs placed near the centre of the tank at a depth of 24 inches, from the cover.

The results show very plainly the advantage of a gas cushion. The pressures with the various depths of gas cushion are shown on the graphs in Figs. 5, 6 and 7. The pressure against the tank

from the same size charge is more than five times as great in the absence of a gas cushion as it is with a 10-inch gas cushion.

In the final tests, charges as much as 480 grams of rifle powder were used. These heavier tests ran very true to form. Those made with gas cushions were not nearly so severe as those without. The outward perceptions confirmed the results shown on the graphs



Explosion Throwing Oil from Completely Filled Tank

of the pressure gauges in no small degree. These latter tests correspond to the most severe types of arcs and approximate more nearly the strength of a secondary explosion.

In all the charges with a gas cushion the relief device was in operation but in the absence of the cushion, the older type relief device was used which was not at all effective. An expansion tank, of the so-called conservator type, was also mounted on the top,

as usual, to take care of the oil overflow. In this case the results of explosion tests were more disastrous than the completely filled tank.

The gas evolved from the combustion of gunpowder (see table) is mostly carbon dioxide and is non-inflammable, so no effort was made to keep the gas cushion oxygen-free.

COMPARISON ARCED OIL GAS WITH THAT OBTAINED FROM POWDER

Material	Carbon Dioxide	Unsat. Hydcbs.	Oxygen	Carbon Monoxide	Hydrogen	Methane	Nitrogen	Hydrogen Sulphide
Transformer oil	.85%	22.8%	2.11%	.80%	65.6%	2.36%	5.6%	——
F. F. F. G. rifle powder	50.63	——	.08	10.47	2.96	.19	33.21	2.45%

In the actual operating Inertaire Transformer,[2] the cushion is kept inert by a chemical compound that robs the air of its oxygen before it gets into the tank. So if an arc rupture occurs and gas is evolved, the cushion absorbs the shock, and when there is no oxygen present a gas explosion is impossible.

In these tests it is well illustrated why so much care was used in selecting the explosion material and the manufacture of the bombs. If part of the charge should fail to fire it would mean a costly repetition and loss of confidence in the work as the charges had to be exact duplicates of each other when making comparisons. The preliminary tests and check tests on the large tank gave the engineers faith in the performance of the explosives.

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[2] "The Inertaire Transformer," Dann and Kellogg.

FUTURE GAS SUPPLY—A CHALLENGE AND AN OPPORTUNITY

By W. M. RUSSELL

Read and discussed before Providence meeting, June 26, 1925

After lying dormant for many years, the business of manufacturing and supplying gas for domestic and industrial purposes is now taking on a new lease of life and it is confidently expected that the next decade will bring an increase in the requirements of gas supply out of all proportion to the existing capacities of plants and distribution stations. This expected great increase in the production of gas will call for tremendous investment in manufacturing plants and distribution systems, and an enormous increase in the consumption of the raw materials which enter into gas manufacture.

The gas engineer will be confronted with two problems—first, the process—and second, the supply of raw material. At the present time there are two widely used processes. The distillation of coal, whether in retorts or in by-product coke ovens, supplies a considerable proportion of the total gas supply of this country, and this process produces, as a residual, valuable by-products in the form of coke and tar. By far the largest amount of gas, however, is made by the so-called "Water Gas" process which utilizes coke or anthracite coal as a fuel wherewith to form blue gas from the action of steam upon it, which is then carburetted or enriched by the addition of oil.

The most immediate pressing problem is the future of the oil supply. Statistics as to the oil supply and consumption of this country have been so commonly quoted as to have become tiresome, and it is not the intention to add anything to the accumulation of such figures. It will be sufficient to quote from the prolific writings about this subject the significant fact that gas oil constitutes about 40 per cent. of the crude oil, and in recent years has produced only about 20 per cent. of the revenue derived from the sale of the products of crude oil, so that the oil man contends that gas oil has never returned its just proportion of revenue in comparison to its proportional production. While the demand for gas oil is increasing at the present time, the proportional demand for gasoline is far out-

stripping the demand for gas oil, and the only opportunity for increasing the yield of gasoline in crude lies in further development of the cracking process. Ten years ago, the average gasoline yield from crude oil was under 20 per cent. There are now 2,500 cracking units in operation, and their operation is so efficient that the average yield of gasoline has risen to 33 per cent. of the crude. As the percentage of recovered gasoline increases, the production of gas and fuel oil proportionately decreases and its price must automatically advance. That this is no dream, every gas engineer can testify when he surveys his gas oil costs for the last ten or fifteen years.

Contemplation of future studies as to the increasing demand for gasoline and the diminishing surplus of gas and fuel oil leads to the conclusion that the time will come when the production of gas oil will practically cease, and the gas engineer must look elsewhere for a fuel to serve the place now filled by that important commodity. The gas industry has not yet reached a point of agreement, or in fact, a willingness to acknowledge the existence of this problem as a whole, but many individuals are fully aware of the situation and a great deal of discussion is taking place and earnest effort is being made to acquaint the industry with the seriousness of the situation and to bring about a realization of the future problems with a view to stimulating engineers and investigators to bring forth new processes which will either require very much smaller volumes of gas oil for a given amount of gas, or which will eliminate its use entirely.

Oil is not the only constituent of gas manufacture which presents a problem. In New England and also in some other parts of the country, anthracite coal has been the standard fuel for water gas manufacture, almost since this process was first introduced. At the present time, few companies can afford to use anthracite coal. Dr. Little is the authority for the statement that there are only 190 tons of anthracite coal in reserve per capita. In spite of the tremendous efforts made to substitute other domestic fuels for anthracite, the consumption of anthracite still goes on, and it will probably continue as a domestic fuel at constantly increasing prices until the reserves are used up—certainly its day as a water gas fuel must pass.

Gas manufacture generally has fallen back upon coke to replace anthracite. Some gas plants manufacture coke and use it in their

water gas machines; others buy their coke. Those companies which buy their coke have a choice of buying the product of Beehive Ovens or By-Product Ovens. Many companies find themselves unable or unwilling to pay the price of coke from By-Product Ovens and have attempted to use the cheaper grades of coke from the Beehive Ovens. This effort has been attended with success at a considerable saving. However, this represents about the last stand in this respect, and it is not thought likely that there is any hope of lower prices for coke for use in water gas machines.

A few companies in this country have undertaken to use bituminous coal in water gas machines, and those using it report success. This is not, however, a logical solution of the problem for, while bituminous coal is cheaper than coke or anthracite, generally speaking, it is not nearly so satisfactory to use—it is difficult to maintain good capacities, and there are troubles and nuisances surrounding the use of bituminous coal; all of which tend to offset the benefits obtained. This criticism, of course, refers to the use of bituminous coal in the ordinary water gas machine in which process most of the coal gas in the gas coal is destroyed and is of little or no benefit to the gas resulting from the gasification of the carbon in the coal with steam and its carburetion with oil.

It is the first thought of many when considering this problem that the proper and easy solution is the further extension of the use of By-Product Coke Ovens or other coking systems. It is probably true that the future supply of many large cities and their suburban territories will be derived from By-Product Coke Ovens. This process has been highly developed and is economical where there is a market for the coke. However, By-Product Coke Ovens offer no solution for the gas company in the average town, as the requirements are all too small to support an institution of this kind. The coke market, while growing, still requires cultivation to secure results. In Massachusetts there is now one large coke producing company, and a gas company is at the present time building a small battery of coke ovens. It is doubtful if any other city in Massachusetts could successfully operate a By-Product Coke Oven Plant. Southern New England is now served by a plant in Providence and another is projected. Most, if not all of the other towns in New England, will have to be served by a process not involving the use of By-Product Ovens. The distillation of coal in retorts does

not afford an economical method of gas supply in commodities of average size. Labor conditions have a great deal to do with this, and any process which involves 24 hour attendance is not looked upon with favor by the managements of small gas companies. This then is the problem confronted by hundreds of gas companies in this country—the gradual disappearance of their supply of oil, and the increasing cost of their coke and anthracite to prohibitive figures.

Aside from the generation of gas, the business of gas manufacture offers many problems. The purification of gas is a chemical process and it has never received the attention from chemists and chemical engineers that other great industrial processes have received in this country. Very recently efforts have been made to eliminate the present cumbersome methods of removal of hydrogen sulphide from gas. These experiments have been, to a great degree, successful, and are highly encouraging, but the field is open and further great improvements are possible.

Until very recently the thought of heating houses and business buildings with gas from the city mains has been considered rather fanciful, but at the present time, the situation is rapidly becoming very different and several large companies are securing great success in heating by gas, utilizing appliances designed expressly for this purpose operating at maximum efficiency. The question of rates has held back the development of heating business, but it is now believed that with an assured market a rate may be expected. This will mean a tremendous increase in the amount of gas required in this country so that the gas industry as a whole is prepared to assume the cost of research and to finance the construction of new plants to meet the changed conditions. The gas industry in general has never received much attention from the chemical engineering profession. There are few mechanical problems which gas engineers have not satisfactorily met, and it is safe to say that any problem which is likely to arise the mechanical engineers can meet, but the chemistry of gas manufacture has not been developed. It is true that the gas industry has not welcomed chemical engineers. Many chemical engineers do not know that there are many opportunities for them in the gas business, and perhaps until recently there have been few opportunities. This situation is entirely changed. The gas industry is now in a position to challenge the chemical engineering profession to solve its problems.

I submit that the solution of these problems offers a great oppor-

tunity for chemical engineers. I do not believe there is any industry in this country which is more ready to receive attention from chemical engineers or which has more problems pressing for solution, or which can offer any greater rewards for inventors and developers of existing or new processes.

I have above stated that one of the greatest problems and opportunities lies in a process of gas manufacture which will utilize bituminous coal with either the admission of very little oil, or eventually no oil whatever.

This process should take bituminous coal capable of coking and containing a rather high volatile content, and completely convert it into a mixture of coal gas and water gas, leaving as a residue only ash and clinker. It should be so designed as to distill all of the coal gas from the gas coal before the resulting coke is gasified by steam in the blue gas section of the process. The coal gas and blue gas should enter the same gas container and be distributed in mixed form. The machine should be so built as to utilize all of the waste heat derived from the process of blowing the coke fire prior to steaming it in making blue gas, and this waste heat should be utilized in some manner to distill the gas coal and form the coke. Equipment should be included to allow of the admission and carburetion of gas oil or in the future of heavy grades of fuel oil. The process must be in a self-contained machine capable of operation by one man, and as nearly automatic in its control and operation as possible. With the present heating value standards, it will be necessary to arrange for the use of some oil, but if all of the coal gas can be distilled and saved, a very considerable proportion of the oil now required would be eliminated.

With the coming of lower B.T.U. standards which many gas engineers recognize as more or less imminent the elimination of that part of the machine having to do with the fixation of oil can be be expected and a very simple process would result.

Such a process capable of operating on the cheaper grades of gas coal now available and designed to handle successfully such heavy grades of oil as are not now considered suitable for gas making would secure the attention and favorable consideration of every gas engineer, and should go far toward solving a great problem of the future gas supply in the average community in the United States.

That this is a great and difficult problem to solve, no one will deny.

Discussion

Arthur D. Little: In view of the challenge contained in the very interesting paper by Mr. Russell, I think you may be interested in some of the results that we have been obtaining in our own laboratory. For some time our attention has been directed toward the problem to which Mr. Russell refers. That is, the probability, or certainty that oil gas will go up in price presumably to a point where the gas man cannot use it as such. I remember that a few years ago gas oil in Boston went as high as 15 cents a gallon, and the gas companies were using three gallons to a thousand feet. Fortunately they had a contract by which they got their supply under the market rate.

When gas oil goes up in price, gasolene will go up in corresponding measure, so that the manufacturer of gasolene will still be enabled to pay the gas oil price. Therefore the problem was to work out a process by which from gas oil a high grade gasolene could be developed in satisfactory amount, and at the same time a large proportion of high B. T. U. gas.

After about three years work we have been able to work out a process which yields not 30 but 45 to 50 per cent of high grade gasoline; a gasoline which has remarkable anti-knock properties, and at the same time a thousand feet or more of gas having a B. T. U. content about 1,700 per cubic foot is made per barrel of oil passed. That gas can be readily passed on to a gas company from a gasoline plant nearby, and used for enrichment purposes. And fortunately the amount of gasoline produced in a plant capable of meeting the enrichment requirements of a gas company would supply only about 15 per cent of the gasoline consumed in that same community, so that there would be no particular disturbance of the market. And the matter has gone further: We have also been able to develop, since this gas contains about 54 per cent of olefines, a whole series of alcohols and other special solvents, and these alcohols are available for many other purposes, as anti-freeze mixtures in the radiators of automobiles propelled by the gasoline. The amount of alcohols so called for is likely to be enormous.

We feel, therefore, that we have a process which has some possibility of relieving to some extent the conditions to which Mr. Russell referred. And since the gas company sells volume and consequently can hardly pay proper rates for the rich gas on the B. T. U. basis, it is also possible by subsequent cracking and increasing this volume, to bring it down to any B. T. U. which may be desired, say 575.

THE STATE VS. INDUSTRY OR THE STATE WITH INDUSTRY

By W. L. STEVENSON

Chief Engineer, Department of Health, Commonwealth of Pennsylvania

Read and discussed before Providence meeting, June 24, 1925

Gifford Pinchot, Governor of Pennsylvania, has said, "Conservation does not mean the holding back of production, it does not mean hoarding. What conservation does mean is the wise use of whatever is to be conserved. The conservation of natural resources which have been given to all the people by the Almighty, means their use in a way that will benefit the greatest number of people for the longest possible time."

For example, it would be futile to have forests from which lumber could not be harvested under proper control and by the same token it would be of no avail to conserve the quantity and quality of streams if thereby they could not be wisely utilized.

The conservation of water resources consists in

(*a*) Regulation for the reduction of floods and increase of the rate of flow during periods of drought.

(*b*) Abatement of harmful pollution and maintenance of cleanly streams in that wholesome state.

(*c*) The allocation of the use so that the greatest benefits are derived therefrom to the greatest number.

The utilization of the water resources consists of the following with the highest use given first:

(*a*) By or for waterworks serving the public for domestic and municipal purposes.

(*b*) For the conveyance of sewage and industrial wastes after suitable treatment, if and where needed, for purposes of sanitation.

(*c*) For water for manufacturing and industrial purposes and for development of power.

(*d*) For navigation.

(*e*) For recreation.

The necessity to erect such principles of conservation and utilization is caused by the intense development of our modern

civilization. When the white man came to America he found vast areas clothed with dense forests and the streams and lakes in their pristine purity, but all practically unutilized.

This natural state was destroyed by the settlement of the country and by civilization. The pioneers hewed down the forests to make clearings for raising their crops, they built their cabins on the banks of the streams and later small towns were established; —still the streams remained fairly clean and pure and their principal use was for navigation and developing power for grist mills.

Later came the devastation of the primaevel forests, great areas put under cultivation, the growth of the towns to cities, the introduction of public water supplies, the use of plumbing fixtures, the installation of sewer systems and consequently the discharge to the streams of the filth of the population as sewage.

Simultaneously, natural resources were developed, such as mines and oil wells, factories were built for the manufacture of finished products from raw materials. All these produced liquid wastes which were generally discharged directly to the streams because it was the easiest way to dispose of them.

Thus, because of the development of the land there occurred the pollution of the streams. The loss of the pristine purity of the streams draining developed areas is the bill which man must pay for the comforts and advantages of modern urban life.

The idealists who demand that all streams be restored to their pristine purity cannot realize their dreams so long as we have cities, industries and cultivated land, because the streams must of necessity receive rain water carrying dirt and filth from the surface of paved areas and the cultivated fields as well as the wastes of domestic life and industrial activity collected by sewers and drains.

However, it is reasonable and generally economically practicable to maintain the now clean relatively small streams in that condition and to restore the majority of moderate size polluted streams to at least reasonable cleanliness. But certain streams draining densely developed industrial areas are in such a condition that they are not and cannot be used other than for disposal of industrial wastes—hence it may not be either wise or economically practicable at this time to attempt their restoration to a cleanly condition.

Many years ago the sewage contamination of public water supplies was found to be one of the major causes of the high typhoid fever rate and also of the frequent epidemics of water borne diseases.

This state of affairs aroused the public and resulted in the enactment of laws by many legislatures vesting in State Health Authorities jurisdiction over public water supplies and the disposal of sewage.

Such statutes frequently provide for the issuance of permits by the State stipulating the conditions under which sewage may be discharged, which in fact means a determination of the degree of treatment needful to safeguard the public health. This and kindred authority created the need for the Sanitary Engineer in public health work and so it has come about that the Bureau of Engineering is an important part of all efficient State Health Departments. The engineer by training is prone to give heed to the economics and practicability of problems of this kind submitted to him for solution.

On the other hand, the discharge of industrial wastes, generally speaking, did not directly affect the public health. Nuisance to sight and smell was created, the water of the stream rendered unfit for many industrial purposes, fish life was destroyed and abutting property values depreciated.

Hence, such legislation as has been enacted concerning the discharge of industrial wastes has frequently been wholly of a prohibitive character, providing for fine or imprisonment but not including provisions for issuance of permits legalizing the discharge where treatment of the wastes, if any, is needed to safeguard public interests. Nor have such industrial waste laws generally been administered by engineers.

The result of the arbitrary enforcement of anti-stream pollution statutes has been to develop a spirit of antagonism between the State authorities and the municipalities and corporations. Therefore, generally speaking, they have not resulted in the rational and sane conservation and utilization of the water resources of the country.

The solution of the problem lies in cooperation instead of antagonism and through adoption of that friendly principle the Sanitary Water Board of Pennsylvania has inaugurated a broad comprehensive program which is already showing results.

This Board was created by the "Administrative Code" of 1923, enacted to reorganize the State Government. It consists of five members of the Governor's Cabinet who are heads of Departments having to do with matters relating to the water resources, such as the Secretary of Health as Chairman, the Secretary of

Forests and Waters, the Fish Commissioner, the Attorney General and the Chairman of the Public Service Commission.

The fundamental resolution of the Board is for the classification of the waters of the State and is as follows:

WHEREAS, The degree of pollution of the waters of the State varies widely from the pristine purity of a small stream flowing through a virgin forest to the grossly polluted stream draining a valley given over to intense municipal and industrial development, and

WHEREAS, Such differences in condition and the present and probable future use of the streams must be recognized in determining the required degree of treatment of sewage and industrial wastes, and

WHEREAS, The natural powers of streams to inoffensively assimilate and dispose of polluting matters by dilution must be utilized so far as compatible with the general interests of the public in order to establish a practicable and economical program for stream control, therefore,

Resolved, That the waters of the State be classified as follows:

Relatively Clean and Pure Streams

Class "A"

Streams in their natural state probably subject to chance contamination by human beings but unpolluted or uncontaminated from any artificial source, hence generally fit for domestic water supply after chlorination, will support fish life and may be safely used for recreational purposes.

Streams in which Pollution Shall be Controlled

Class "B"

Streams more or less polluted, where the extent of regulation, control, or elimination of pollution will be determined by a consideration of (*a*) The present and probable future use and conditions of the stream; (*b*) the practicability of remedial measures for abatement of pollution, and (*c*) the general interests of the public through the protection of the public health, the health of animals, fish and aquatic life, and the use of the stream for recreational purposes.

Class "C"

Streams now so polluted that they cannot be used as sources of public water supplies, will not support fish life and are not used for recreational purposes and also from the standpoint of the public interests and practicability it is not now necessary, economical or advisable to attempt to restore them to a clean condition; and further,

Resolved, That all artificial pollution of Class "A" streams shall be prohibited and any sewage or industrial wastes on the watershed shall be treated to such a degree that the effluent shall be practically free from suspended matter, non-putrescent and disinfected and that recreational use shall not be sanctioned within prejudicial influence of water works' intakes, and further,

Resolved, That the degree of treatment of sewage and industrial wastes discharged into Class "B" streams shall be determined for each particular stream or portion thereof after consideration of the general interests of the public and the economics of the particular case, and further,

Resolved, That sewage and industrial wastes may be discharged into Class "C" streams, provided, however, that such discharge shall not create any public nuisance or menace to health.

It will be noted that this establishes principles both of conservation and wise and controlled utilization. It recognizes the natural powers of streams to inoffensively assimilate and dispose of polluting matters by dilution but imposes the limitation that such powers shall not be abused to the harm of the public interests.

In dealing with the problem of proper disposal of municipal sewage the Board does not, except in most unusual cases, issue peremptory and arbitrary orders to a town demanding the immediate construction of a complete system of intercepting sewers, and sewage purification works. Instead it causes a survey to be made to ascertain the present and probable future use and condition of the stream which receives the town's sewage and based thereon determines the minimum degree of treatment deemed necessary to maintain the stream in a condition fit and suitable for its uses.

Then by conference between the engineers of the State and of the municipality, a financial program is determined upon for the progressive construction of the works required to bring about the interception and required degree of treatment of the sewage. This program when adopted by the town council is submitted to the Sanitary Water Board and if they find it to subserve the public interests, it is approved and the work proceeds thereunder.

The Board offers the industries of Pennsylvania the same spirit of cooperation and already has had noteworthy success, e.g., with the leather tanning companies operating in Pennsylvania.

The pollution of streams by tannery wastes has been a most vexatious problem, there appearing up to the present to be no reasonable remedy at hand. Several companies have spent considerable sums of money for the construction of treatment works

which proved to be inefficient and results attained by no means commensurate with the cost.

The Bureau of Engineering invited the engineers and chemists of certain of the largest tanning companies to a conference at which it became clearly evident that neither the State nor the industry had scientific worthwhile data concerning the amount of tannery waste which streams can inoffensively assimilate nor of reasonable and practicable ways and means for the treatment of tannery waste to various degrees so that the effluent could be safely discharged to the streams.

The outcome of this conference was another one between the Sanitary Water Board and the executives of the leather tanning companies at which a form of agreement was approved and which was subsequently executed by practically all of the companies operating tanneries not in municipalities having sewer systems to which they have connections.

This agreement provides for the creation of a fund of $35,000 by contributions from the companies in proportion to their rated capacity in pounds of green salted hides a day.

This fund is being expended by a committee consisting of three engineers and three chemists who are employes of participating companies and the Chief Engineer of the Sanitary Water Board, as Chairman.

The agreement provides for the construction and operation of a full-scale experimental treatment works by the committee and that if reasonable and practicable methods are found and approved by the Sanitary Water Board their installation at any tannery will be deemed compliance with the anti-stream pollution laws.

The Committee selected a tannery at Instanter, Elk County, Pa., as the site for the experiments because the stream now receiving that tannery's waste is not otherwise used or polluted for several miles and hence provides means for study of effect of various ratios of discharge of tannery waste both untreated and treated to various degrees.

Gauging stations have been established to give the rate of stream flow at various points and sampling stations selected.

The first work of the committee was to determine the rate and times of production and, by analyses, the chemical and physical characteristics of the 16 separate ingredients of the combined tannery wastes.

These studies indicate that if certain of the intermittently produced acid and alkaline wastes are mixed together and allowed to naturally react upon one another that a heavy precipitant forms including considerable material originally in solution and that the supernatant liquor is markedly lighter in color than the combined wastes.

These reactions promise sufficient success in preparation of the wastes for treatment that the Committee has approved plans for constructing the first part of the experimental plant in order to try out the laboratory procedure on full scale.

The program includes finding the maximum ratio at which untreated tannery waste can be disposed of in streams for application in cases of tanneries situate on large rivers. Also the ratio for tannery waste treated to various and increasing degrees of purification so that for any given rate of flow of stream and its use it will be known to what degree it need be treated and how to do so at the least expense.

While the Sanitary Water Board has thus been cooperating with industry, in a neighboring state a bill was introduced in the legislature containing most drastic penalties for industrial pollution of streams and the District Engineers of the United States Army are gathering data for a report by the Secretary of War to the Congress relative to Federal control of stream pollution.

The universal use of the automobile is taking the city dweller far afield into the country, the mountains and the woods. Outdoor swimming pools, tourists camps, hunting and fishing are all becoming more and more popular.

The result is an insistent demand upon the part of the public for absolutely clean streams. They used to be grieved and offended by gross stream pollution. Now they are outraged by all visible evidences of any pollution of streams where they desire to find recreation.

So industry is confronted with possible jurisdiction of the Federal Government or drastic state legislation to estop all discharge of industrial waste without complete treatment.

The policy of the Sanitary Water Board of Pennsylvania offers a way out of the dilemma—to wit: conservation and utilization; cooperation in a scientific manner to secure permanent, reasonable results instead of antagonism and litigation.

It is for industry to choose but it might be well to remember that the days of "the public be damned" attitude are of the past and a new order has arisen.

Discussion

Mr. Stevenson (Continuing): The State of Ohio through Dr. Monger, Director of Health, and Mr. Dittoe, Chief Engineer, have, like Pennsylvania, inaugurated a campaign for abatement of pollution of steams through cooperation. In the last Ohio Legislature a bill was introduced at the request of the Director of Health giving to the State Department of Health very full and complete control over stream pollution including the issue of permits, and the manufacturers of Ohio joined with the Department to put the bill through the Legislature, apparently because they prefer to deal with the Health Department and its engineers.

Dr. Charles L. Reese: Gentlemen, this is a very interesting paper and brings before us a question which is extremely important to the chemical industries in this country. The subject of "Centralization" which President Coolidge is trying in all his speeches to avoid, and the handling of streams by the War Department, is a very dangerous thing. The War Department is endeavoring to get control of all streams on account of their present control of navigable waters. We must fight that and keep the control in the state where it belongs, because as Mr. Stevenson has said, the states are the local people interested in the industries in the state, and by cooperating with the State authorities we should have no trouble.

The United States Congress is very likely to bring up bills on stream pollution throughout the country, and all the states are doing the same thing, so that our duty is to try to guide that legislation in the right direction.

As a matter of fact, I do not believe we need any laws. The medical laws take care of the thing so far as the nuisance is concerned. But it is coming and I think we have got to consider it. I am glad that Pennsylvania is acting in such a wise way and I think we are indebted particularly to Mr. Stevenson for his presentation of the matter here.

E. B. Besselievre: Mr. Stevenson brings out the point of allocation of streams to industrial waste discharge. That same question was raised on Wednesday by one of the speakers after Mr. DeLaporte of the Provincial Board of Health of Ontario, had said that they were doing the same thing up there. The question at that time was whether the State would guarantee to the industry which it allocated to a certain stream for the discharge of waste,

that they would not in future have to put in treatment works when conditions had changed, when the stream was needed for water supply or some other purpose. I do not know whether Mr. Stevenson can give us some information on that or not. Dr. McKee asked the question on Wednesday.

Mr. Stevenson: Gentlemen, I think the question was answered in the resolution which I read before, where reference is made to "the present and probable future use and the condition of the stream." Also the statement that the use of the stream for water supply purposes is the first and highest use. I do not think that the State ever ought to issue irrevocable permits in perpetuity. The tendency of modern government is against it. Franchises are no longer issued in perpetuity, and the higher use should always be able to capture the lower use. I cannot commit the Sanitary Water Board, but speaking for myself I would not favor the issue of a permit granting authority to discharge untreated industrial waste for all time to come, lest future generations be deprived of rights to which they are entitled. Does that answer your question?

Dr. Ralph H. McKee: The question is really this, to express it in a concrete case; that if they adopt certain schemes it will be taken as meeting the needs, and that they will be relieved from further criticism. Is it understood there that this will be for a definite time, 10 or 25 years, and in that respect like an ordinary franchise? Or in the other case, will it mean a permanent meeting of the requirements unless some radical or unexpected new demand on the stream arises, such as a water supply not anticipated at all, but not counting for example such things as good fishing or bathing purposes,—sport purposes, we will say? Has the Board considered those, and what does it mean when it says it will grant immunity for a time?

Mr. Stevenson: Navigation in the early days of this country was the highest use of streams. It was the means of communication from place to place, and needed for the movement of goods. But navigation is now near the end of the list, with recreation below.

But specifically answering your question,—in Pennsylvania the existing statutes give the state authorities the right to issue sewerage permits, and to stipulate therein the conditions under which the sewage may be discharged. When those permits are issued for discharge of untreated sewage, they are for a limited time, usually two years. Upon application they are renewed, and this renewal

has been going on since 1905 when the statute was first passed, and I presume will be continued on rivers large enough to assimilate the sewage, and where it does not threaten a water supply below.

We lack at the present time statutory authority to issue permits for industrial waste. A bill was introduced in the last Legislature at the request of the Sanitary Water Board, to give it the same power to issue permits for industrial waste as for sewage. Curiously, and I cannot tell you why, industry did not seem to see the advantages which would accrue to it, but one very large interest had the bill so amended that it became necessary to withdraw the bill.

The Board should have the power to issue permits for industrial waste, treated or untreated so as to give industry the same protection that municipalities now have, because when a permit is issued to a municipality for discharge of sewage, it estops the state from action so long as the terms of the permit are faithfully complied with. If the Board had the same authority to issue permits for industrial waste, I believe it would be to the interest of industry. I doubt very much if it would stop the down stream riparian owners from bringing suit, but it would have the advantage of showing that the use of the stream was in accordance with a policy which had been adopted by the State authorities, and that would have weight with the court as against complaint of a private owner.

Dr. McKee: Take the case of the tannery that you are working on, whether a tannery which may go to extraordinary expense in installing the plant may, with the change in the Board of Health a little later, be protected against what might be spoken of as a change of opinion. At present there is no protection as I understand.

Mr. Stevenson: No. The agreement of July 30, 1924, made between the Sanitary Water Board and the leather tanning companies, provides for investigations, and if we determine reasonable and practical means for treatment of tannery waste, then the installation of such approved methods at any tannery will be deemed compliance with the law. That is as far as I can say.

Robert S. Weston: I think we are to be congratulated to have Mr. Stevenson present this excellent statement. Of course we know that in a frequently cited Massachusetts decision (Parker *vs.* American Woolen Company), it is stated that the riparian owner is entitled to reasonable use of a stream and Mr. Stevenson has gone a long way toward defining the reasonableness.

The point in his paper which ought to be emphasized is the classification of streams. A river like the Moshassuck, which is used for manufacturing and flows into Providence harbor, is to be treated very differently from the upper Pawtuxet River which is to be used for water supply for the city of Providence. Then there are cases under Federal control where pollution in one state may affect the water supply in some other state below, and some way must be found by gentlemen's agreement or otherwise, to care for these cases in case state river control is continued. One case in mind is the Ten Mile River, which supplies the city of East Providence across the Seekonk River with water. Above the water works is the large manufacturing city of Attleboro, and the town of North Attleboro, both in Massachusetts. Both fortunately have good sewage disposal plants, but the river is nevertheless carrying quite a load of pollution from various sources.

Another factor is the effect of automobile touring on streams,—the effect of migratory population. Formerly many of our city water supplies were adequately protected by the purchase of land about their sources. Now, in many cases, highways are built crossing these reservations, and the automobile brings crowds of pleasuring people to the catchment areas for week-ends. Sometimes it has been necessary to establish camp sites which may be used without damage and entice the picknickers away from dangerous locations. It is usual to provide these places with fireplaces, incinerators, water, privies and other facilities in order to keep people away from the banks of the streams.

The question of stream control is an important one, and those of us who are concerned with it professionally are very glad that Mr. Stevenson has given such a clear presentation of the State's point of view, and taken so sound positions.

Mr. Besselievre: A question was asked on Wednesday by Dr. White. Will you repeat that question?

Dr. A. H. White: I think it has been answered largely. I was speaking of the future trend of legislation. I have understood that the states are making greater and greater demand for purification of streams, and legislation is becoming more and more drastic. In Michigan there is talk of private suits being brought, and I wanted this information which Mr. Stevenson has given to you about what is being done specifically in Pennsylvania, and I think I understood from the full discussion that the manufacture in more

states are gradually coming together on these problems. The future success in this line must be through agreement, because it is realized that if there is not agreement there will be legal enactments which may be pretty oppressive. Is that not the trend of opinion, Mr. Stevenson?

Mr. Stevenson: I think you have expressed the thought in my mind. There is no doubt that popular demand is arising for very drastic legislation, and as soon as that demand is strong enough on the representatives in our Legislative bodies, they will enact stringent laws. But that can be avoided by industry through cooperation with the proper state authorities.

I would like to refer to one remark of Mr. Besselievre, namely, the question of pollution of interstate streams.

Several years ago the Federal Government, through the War Department and the United States Public Health Service seemed to advocate Federal control of interstate streams. I think Pennsylvania has shown that it is unnecessary. In 1922 the State Health Departments of New Jersey and Pennsylvania entered into an agreement setting up standards for treatment of sewage before discharge to the Delaware river. It set up high standards for the upper part of the river where there is little industry at the present time. It set up lower standards for the lower portion of the river. That agreement has been of great advantage to both States because it has meant that one state cannot discharge an improperly treated or undue amount of sewage while the other state is obliged to go to an unreasonable expense.

The Health Departments of Pennsylvania, Ohio, and West Virginia entered into an interstate stream agreement in 1924, which is not specific in its terms, but is an agreement of the three departments to cooperate with each other, to carry out a uniform policy of conservation in the interstate streams.

In 1925, the Commissioners appointed by the Governors of Pennsylvania, New York and New Jersey negotiated a compact as to the Delaware River. Article 10 of that compact sets up specific degrees of treatment of sewage before discharge to the Delaware River, which is a boundary stream, all practically in accord with the New Jersey-Pennsylvania agreement of 1922. The tributaries of the Delaware River lie in the separate states and the compact holds each state responsible for administering its laws so as to bring about the condition that the sanitary quality of the tributary at the

point of confluence shall be no less than the sanitary quality of the river itself immediately above. In other words, the tributary stream shall not harm the Delaware River.

A little later another agreement was executed by the Health Departments of Pennsylvania and New York, similar to that made between Pennsylvania, Ohio, and West Virginia, namely, that they shall cooperate in conservation of interstate streams. So you see Pennsylvania has surrounded herself with agreements as to interstate streams, and has met fairly the question of interstate stream control.

Dr. N. K. Chaney: May I ask Mr. Stevenson, what is your experience with this form of interstate stream control in states having a dual relationship to the stream, whether you believe it would be applicable to a large number of states like those in the Mississippi River Valley and Missouri River Valley. I think that would be a case where the looseness of your gentlemen's agreement, and the difference between the interests of those states at the head of the stream and those at the foot. might lead to some pretty serious difficulty.

Mr. Stevenson: I think that in the case you cite, it is impracticable. However, on the Colorado River, which has a very large watershed, eleven states have entered into a compact which has been ratified by ten, and the eleventh has it still under consideration. In that case eleven states entered into one compact.

E. B. Besselievre: I think that one of the most important things that Mr. Stevenson has said this morning was that they recognize in Pennsylvania the fact that they should advise the town of the *minimum* degree of treatment that they may go into. I do not know whether in the law that they contemplate getting for control of industrial waste, they have incorporated that idea, but it is a very important thought particularly for the industry which has to treat its waste. In most of the states which insist on treatment of industrial waste, they simply tell the manufacturer that he must treat his waste so as not to pollute the stream, but do not tell him how far he must go. It means a great difference in expense to the industrial operator. If he can find out that he does not have to provide complete treatment, but can stop half way or at some intermediate point, it would be very satisfactory. Most of the industrial waste treatment plants are chemical installations completely or partially, and if a manufacturer has to saddle himself

with a large expense simply because the State has not defined the limits of treatment, he has burdened himself with an expense not necessary. If as in Pennsylvania in the treatment of sewage, they will at the same time designate the extent to which the industrial waste must be purified, then they will be doing a great work.

MR. STEVENSON: Municipalities and industries are entitled to be notified of any requirement which is to be hoped for the treatment of waste. The purpose of that is, after investigations have been made, maps can be prepared indicating the degree of treatment required, and then an industry would know whether it is wise or unwise to locate on that stream.

ROBERT S. WESTON: What would naturally be the policy of such a board in Pennsylvania regarding waste whose treatment has not been worked out, like wool scouring waste which has to be discharged either as a partially degreased effluent, or as an effluent containing sulphuric acid? Here in Rhode Island, the problems are being worked out in what seems to be a very satisfactory way by the getting together of the manufacturers and the people. Rhode Island, as you know, is a manufacturing state above everything else. Probably more than $750,000,000 a year of its income is from manufacturing while that from farming is less than $6,000,000, and from fisheries less than $5,000,000. Yet the urge toward purification of streams comes from the fishing industry, which includes the oyster industry.

Finally the public-spirited manufacturers got behind a bill to establish a Board of Purification of Waters in this state. So far their policy has been largely educational, and they have placed no burden upon any manufacturer which has been unwarranted by the facts. The manufacturers have done everything that they could to cooperate, and this state is an example of reasonable progress along those lines.

MR. STEVENSON: Answering Mr. Weston, please note in the definition of Class "B," that it says: "where the extent of regulation, control, or elimination of pollution will be determined by a consideration of (*a*) The present and probable future use and conditions of the stream; (*b*) The practicability of remedial measures for abatement of pollution."

At the present time I do not know a reasonable and practical causes for treating sulphite pulp waste. That would indicate to me that if sulphite pulp waste were discharged into a certain stream it

would be unjust to expect an industry situated on that stream to treat their waste to a higher degree, in order to allow the sulphite pulp waste to flow into the stream without creating a gross pollution. That simply would not be just.

MR. CUNNINGHAM: May I ask to what extent The Sanitary Water Board has complete control of stream pollution? Ten years ago the Department of Fisheries and Department of Health had control of the fisheries and rulings of the Department of Health were often antagonistic to those of the Department of Fisheries.

MR. STEVENSON: Prior to the enactment of the so-called "Administrative Code" by the Legislature of 1923, the Board of Fish Commissioners administered all the fish laws including Section 100 of the so-called Fish Law of 1917, which prohibits the discharge into streams of any matter deleterious to fish. In 1905 jurisdiction over sewage was vested in the Department of Health. In 1923 there was created the Sanitary Water Board consisting of the Secretary of Health, the Attorney-General, the Secretary of Forests and Waters, the Fish Commissioner, and the Chariman of the Public Service Commission, and all anti-pollution laws were transferred from their former administrators to this Board. The Sanitary Water Board therefore administers all anti-stream-pollution laws.

ANTHONY V. DELAPORTE: Comments on Mr. Stevenson's excellent paper are unnecessary. There are two points, however, in which our Ontario practice might be of interest. There has been some interest expressed here in the lobbying by the Izaak Walton Club. Our tenure of office up there is more or less secure during the life and good conduct of the official, and so we do not worry much. A Board of Health does not change, although the Legislature does change. We have had the same Board of Health ever since I can remember, and none have died within the last few years. They can act fearlessly and trample on the toes of anyone who is not living up to the Regulations, or if a manufacturer is being persecuted for selfish interests, protect him.

The Act specifically states that all our local officers of Health are protected the same way. A local officer cannot be removed from office except with the consent of the Department of Health, of the Province of Ontario.

To meet your Isaac Walton situation we have what we call a playground in Ontario. The northern part of the Province of Ontario is a vast area of rivers and streams where are lots of fish.

There is now no pollution at all, practically, and none would be tolerated.

Our touring agencies and the railways arrange so that the Isaac Waltons get up to this section and not on the polluted streams. When an Isaac Walton gets on a polluted stream, it is a mischance.

When, in regard to the method of treatment, of tannery waste, we have found that we can get a lime sludge which is very valuable as fertilizer. It is said that it will raise grass when nothing else will. The effluent has a slight odor and a slight color.

We have just completed a series of experiments in which Mr. Stevenson might be interested.

At the city of Kitchener a small activated sludge tank was installed—by an arrangement of pumps we could feed any proportional amount of tannery waste to the domestic sewage. We found that we can treat a mixture of 50 per cent tannery waste and 50 per cent domestic sewage in an activated sludge tank and get a purification of over 90 per cent. The effluent is practically free from color and can be discharged without fear of nuisance. With mixtures containing over 50 per cent tannery waste, the results are not so good, although in an emergency up to 60 per cent could be treated.

STATUTORY REGULATION OF STREAM POLLUTION AND THE COMMON LAW

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Read and discussed before Providence meeting, June 24, 1925

The basic rule of the common law has been stated to be that each riparian proprietor has the right to have the stream come down to him with its quality unimpaired and with its quantity undiminished.

Due to the necessities of the commercial activities of modern civilization, this rule has been modified to allow reasonable use of the stream by proprietors above him.

What constitutes reasonable use is a question that has been carried into many courts and has resulted in much legislation for the control of the abuse of streams as depositories for industrial wastes. Many of these laws are wise and, when properly administered, enhance the public good. Others are pernicious in principle and work only for the benefit of a favored few, and, unless judicious administration is possible, injury to health and property may result from their enforcement.

It is not the intention to cover in this paper the many problems and phases of stream pollution from industrial wastes, but to present in brief form a resume of the legislation, restrictive, or regulatory, as promulgated by the several States.

Most of the United States and the Provinces of Canada now have duly constituted, official health agencies, usually called a Department, or Board, of Health, with the necessary equipment and machinery and trained personnel provided for the intelligent and satisfactory administration of the health laws. The general health laws, themselves, are usually creatures of the legislative bodies of the several States.

Some States attempt to draft a complete health law, leaving the Health Department little leeway in its administration. Others, for instance Massachusetts, leave to the Health Board the details of the legislation, allowing this Board to recommend laws, to cover specific cases of pollution, or for the control of unique or unusual

problems. As the Health Board is usually constituted of trained medical and sanitary experts, this would seem to be the most logical procedure and the one which would lead to the greatest good for the greatest number.

What constitutes pollution of a stream is also a mooted point, and is a local problem to which no general rule or law can be applied. In some instances, the discharge of the wastes from *any* type of industrial plant into a stream which is used, without further treatment, for the water supply of humans, must not be permitted; while, in other instances, the use of a stream for carrying the liquid discharges of a number of plants is not at all objectionable.

Some streams have been so long used as carriers of industrial wastes, that it would not be economically practicable to require the elimination of all wastes, or to attempt to use the streams for potable water supply. Other streams, mildly polluted, may be potential sources of water supply for growing districts, and, if the industrial waste flow is not large, these streams may be reclaimed and either complete or partial treatment given the wastes before discharge into them.

Pennsylvania has taken the lead in recognizing the basic rights given by long continued usage, and has taken into consideration the economic feature of compelling complete reclamation of a stream, as against the enormous cost to the industries of accomplishing this. In its recently enacted legislation, creating a Water Board to have jurisdiction over all intra-state waters, the streams of the State were divided into three classes, first, those that are so grossly polluted as not to be worthy of consideration as sources of potable water supply and may continue to be used as carriers for industrial wastes; second, those that may in the future become necessary to furnish human water supply, and where the exclusion of certain toxic wastes, or partial treatment, must be resorted to before the discharge of the wastes; and third, those which are now used and will be increasingly used for human water supply, and from which all wastes must be excluded or completely treated before their discharge.

A recent case that has been widely discussed is that of the Passaic River in New Jersey, which, for many years, has been so grossly polluted by numerous cities and several hundred industrial plants of all kinds that it was a visual and nasal nuisance. In June of 1924, the large Passaic Valley Trunk sewer was put into service,

the object being to take all of the municipal sewage, and as much as possible of the industrial wastes, through this sewer, so as to avoid the continued pollution of the stream. All of the cities along the line of the river are now discharging their sewage into this sewer, and already there is a noticeable improvement in the stream. On the other hand, the quantities of wastes have increased so much since the sewer was designed, that it is impossible for the Commission to take all of these wastes into the sewer, and it has been necessary to restrict the industrial waste contribution to approximately ten percent of its volume.

In this case in particular, there comes up the question of the inherent right of riparian owners to the undiminished flow in the stream. Practically all of the many industrial plants take their water from the Passaic River, and, as many of them use enormous volumes each day, several of the plants requiring from ten to fifteen million gallons, each, the permanent removal of all of this water from the river flow and its discharge into the sewer would ultimately result in a dry stream bed. Consequently, it has been recognized that one of the basic duties of the Commission is to maintain sufficient flow in the river to produce a considerable volume. This means that, in principle, a manufacturer may discharge ten per cent of his wastes into the sewer and the balance into the river, so treating the polluting wastes that the river will be restored to a condition where it is not obnoxious to sight or smell.

Competition is keen in modern business, and every expense added to the cost of production of an article handicaps the manufacturer in his sales' efforts, or reduces his profits. Consequently, a manufacturer discharging a polluting waste into a stream naturally staves off the evil day of treatment as long as possible, particularly if his most ardent competitor is situated below him on the same stream, or elsewhere, where treatment of *his* wastes may not be required. The manufacturer cannot be blamed for this attitude, but it has been decided in the courts that "the fact that others than the defendant, or even the plaintiff himself, are polluting the same stream, will not excuse the defendant."

It is unfortunate that the treatment of industrial wastes, in all but a very few isolated cases, can only be looked upon as an expense. Vain hopes have been held out to manufacturers that, as their wastes contained chemical products, greases, fats, acids, and other constituents, which had a potential value, these wastes could

be treated so as to recover these materials and produce a revenue that would either pay a profit or at least offset the expense of the treatment.

Many manufacturers have learned, to their sorrow, that the cases where this can actually be accomplished in practice are few and far between, and that the cost of recovering the products, in a state ready for market, is usually more than the market price of the products themselves.

Manufacturers must recognize the fact that, if they are required to provide treatment works for their wastes, it is far better to attack this problem from the primary viewpoint of preventing pollution and let the possible profit from recovered products be secondary, or a possible pleasant surprise.

There are, of course, two sides to this question, as to all others. The viewpoint of the manufacturer, required to provide treatment of his works, should be to comply with the request and to cooperate with the official or body having jurisdiction. The other side, the compelling authority, should not arbitrarily issue an order for eliminating pollution, without a careful and full statement of the case. The manufacturer is entitled to know, and can rightly demand to be advised, of the extent to which his wastes must be treated, and should be given the benefit of any experience which the health engineers have, as to how it may be done. Industrial waste treatment, particularly in the United States, is a new field of sanitary engineering and very little is known of the most economical and efficient way to treat some classes of wastes.

The degree of treatment required for a given industrial waste depends upon several conditions, all of prime importance.

In every case, the manufacturer after being advised by the health official of the degree of treatment required, should call upon some experienced engineer, or engineering organization specializing in industrial waste treatment, to investigate his problem, make the necessary tests and analyses, and to work out the most economical form of treatment that will produce an effluent that will be satisfactory to the health authorities. In many cases, the manufacturer has his own chemists and engineers, and these men usually have intimate knowledge of plant processes and conditions, that will assist the expert in a more rapid and satisfactory solution of the problem. Complete cooperation between the plant chemist and the consultant should be insisted upon by the manufacturer, the one whose pocket-book will be most affected.

Including the basic rule of the common law as given in the beginning of this paper, there are about forty of these rules upon which the courts of justice have laid their decisions in a long list of litigations for pollution by industrial wastes. These rules are given in brief, herewith; and if more detailed information is wanted upon the actual decisions, this may be readily procured.[1]

2. As each riparian proprietor has a dual interest in the stream, it logically and necessarily follows that each riparian proprietor is permitted to make a reasonable use of the stream, and no more.

3. The true rule may be stated to be that each riparian proprietor has the right to have the stream flow through, or past, his land, with its quality unimpaired and its quantity undiminished, except in such manner and to such extent as may result from a reasonable use of the stream by riparian proprietors above him.

4. Courts have generally favored those uses of a stream that may be classed as natural, such as domestic use, watering of cattle, etc., as distinguished from artificial uses, like manufacturing.

5. But, although a use may be classed as a natural one, if it be exercised immoderately or excessively, it becomes unreasonable and illegal.

6. Ordinarily, the drainage of surface water cannot be made the ground of complaint, even though it causes injury to a lower riparian proprietor.

7. While the riparian proprietor may accelerate the runoff of surface water into a natural stream, he will not be permitted to divert it from its natural course.

8. Discharging waste from a manufacturing plant, or mine, into a stream is not a natural use of the stream, and, if done to the material injury of the lower riparian proprietor, creates a liability for damages.

9. The fact that a manufacturer is engaged in an important industry, the operation of which benefits the public, will not be held to excuse him for polluting the stream to the injury of the lower proprietor.

10. Even where a lower proprietor can, at comparatively small expense, protect himself against the injury caused by an upper proprietor engaged in an important business, he is not bound to do so.

[1] Public Health Bulletin No. 87, "Stream Pollution. A Digest of Judicial Decisions and a Compilation of Legislation Relating to the Subject." Superintendent of Documents. Washington, D. C. 30 cents.

11. The doctrine as to mining wastes, covered by the Sanderson case, holds only in Pennsylvania and Indiana, and is expressly repudiated elsewhere.

12. Evidence of the custom of the region in which the stream is located may be relevant as bearing upon the reasonableness of a given use.

13. It has been intimated that new and unusual uses will be regarded more jealously than common and customary ones.

14. The fact that others than the defendant, or even the plaintiff himself, are polluting the same stream will not excuse the defendant.

15. Evidence that others than the defendant have contributed to the pollution of a stream is admissible for the purpose of showing that not all the damage sustained by the plaintiff was caused by the defendant.

16. Where a stream has been polluted from various causes, for longer than a prescriptive period, to such an extent that it has become a common sewer, the right to pollute it cannot be challenged.

17. When a stream is polluted by an upper riparian owner in an unreasonable way, or to an unreasonable extent, any lower riparian proprietor who is injured thereby has a right of action at common law, for the actual damages sustained by him.

18. It is improper in an action for damages for several riparian proprietors to join as plaintiffs. Each should sue separately for the damages he has sustained.

19. It has been held to be improper to join several defendants in an action for damages arising from the pollution of a stream to which the various defendants have contributed independently.

20. On the other hand, several decisions to the contrary have been given, the reasoning being that it is impossible to separate the injury done by the several contributors, and that to deny their liability is to leave the lower proprietor without remedy for the injury he has sustained.

21. Where the cause of injury to a stream has been maintained by consecutive proprietors, the proprietor furthest downstream will not be permitted to take joint action against them for damages, but must sue each separately.

22. An unreasonable use of a stream which pollutes it to the injury of a lower riparian proprietor will be enjoined.

23. Several who contribute individually to the pollution of

the same stream may be joined as defendants in one suit for an injunction.

24. Several individuals who are injured by the pollution of the same stream may join in an action for an injunction.

25. To entitle a riparian owner to an injunction against polluting a stream the injury of which he complains must be real and material.

26. But, although the injury to the stream must be real in order to entitle the plaintiff to injunctive relief, it does not follow that the plaintiff must have suffered any actual damage in his present use of the stream.

27. In suits for injunction against pollution of streams, the general rule that a nuisance will not be enjoined in an equity suit, until its existence has first been established in an action at law, does not obtain, the reason being that the delay incident to the establishing of the right in an action at law might cause irreparable injury.

28. Where the effect produced by the pollution of a stream amounts to a public nuisance, the State through its attorney general may bring action for an injunction against the continuance of the pollution.

29. As against a lower riparian proprietor, a right to pollute a stream may be acquired by prescription.

30. A right to create a public nuisance cannot, however, be acquired even by prescription.

31. A right by prescription cannot be acquired to authorize the doing of anything that is forbidden by statute.

32. By the great weight of authority, municipalities have no greater rights than individuals to pollute watercourses, and must respond in damages for any injury caused to a lower riparian proprietor, and may be enjoined from continuing the pollution.

33. At common law, a city seeking to maintain the purity of a stream, as a lower riparian proprietor, has no greater right than an individual to limit the use of the stream by upper proprietors.

34. To protect its streams against pollution, a State may, without providing compensation, curtail the rights of the riparian owner in his use of the stream, according to the weight of authority.

35. Even though a riparian owner may have acquired a right by prescription, to pollute a stream, as against the lower proprietors on the stream, he is nevertheless amenable to legislation enacted under the police power, for the preservation of the purity of the

stream, and cannot claim compensation unless it is provided in the legislation.

36. Such legislation is not rendered invalid by the fact that it is made applicable to a portion of the State only, provided no unreasonable or arbitrary classification be adopted.

37. Some courts have held that statutes enacted for the preservation of streams should be liberally construed in favor of the riparian owner.

38. A State may leave, to a commission or board, the details of legislation for protection of its waters.

39. The power of the State to authorize the discharge of sewage into streams, to the injury of lower proprietors, is limited by constitutional provisions.

As the manufacturer is usually interested, particularly, in the law which governs his case, the writer has prepared the following table for ready reference, which shows, by States, the general scope of the health law, whether specific industries are cited or exempted, and whether penalties are imposed for non-compliance.

Careful inspection of the available information shows that forty-seven of the United States, four of the Provinces of Canada, and Hawaii, Porto Rico, and the Philippine Islands, and the District of Columbia, have general health laws governing pollution of waters by industrial wastes.

New Hampshire started the ball rolling by passing a law of this character in 1892, followed rapidly by the other States.

All of the States, and other divisions mentioned, provide penalties in fines ranging from $10.00 to $5,000.00, or imprisonment of from ten days to a year, or both, for failure to comply with the regulations of the health authority having jurisdiction.

Thirty-eight of the United States mention, specifically, certain classes of wastes which must be excluded, and all of them cover the ones not mentioned, by a general clause referring to "wastes from any manufacturing plant" or "wastes containing any harmful or deleterious substance."

Twelve of the States provide exemption for specific industries, varying from the mining and tannery wastes in Pennsylvania to the "retting of maguey, sisal, etc." in the Philippine Islands; but, regardless of these exemptions, in each case there are clauses, in later laws, which practically nullify the exemption where damage can be shown.

States Having Health Laws Governing Pollution of Streams by Industrial Wastes

Year in which Law Took Effect	State or Territory	Law Covers Industrial Wastes	Specific Industries Named on Certain Streams	Certain Industries on Streams Exempted	Penalty Provided for Violation
1907	Alabama	x	—	—	x
1913	Alaska	x	x	—	x
1913	Arizona	x	—	—	x
1916	Arkansas	x	—	—	x
1915	California	x	x	—	x
1913	Colorado	x	x	x	x
1902	Connecticut	x	—	—	x
1915	Delaware	x	x	—	x
1911	Dist. of Columbia	x	x	—	x
1914	Florida	x	x	x	x
1914	Georgia	x	x	—	—
1905	Idaho	x	x	x	x
1917	Illinois	x	—	—	x
1914	Indiana	x	x	—	x
1897	Iowa	x	—	—	x
1915	Kansas	x	x	—	—
1912	Louisiana	x	x	x	x
1903	Maine	x	x	—	x
1914	Maryland	x	x	x	x
1902	Massachusetts	x	x	—	x
1912	Michigan	x	—	x	x
1913	Minnesota	x	x	—	x
1906	Mississippi	x	x	—	x
1909	Missouri	x	x	—	x
1907	Montana	x	x	—	x
1913	Nebraska	x	x	—	x
1912	Nevada	x	x	—	x
1892	New Hampshire	x	—	x	x
1910	New Jersey	x	x	—	x
1915	New Mexico	x	x	—	x
1911	New York	x	x	x	x
1908	North Carolina	x	x	x	x
1913	North Dakota	x	x	—	x
1912	Ohio	x	x	—	x
1910	Oklahoma	x	x	—	x
1910	Oregon	x	x	—	x
1915	Pennsylvania	x	x	x	x
1908	Philippine Islands	x	—	x	x
1911	Porto Rico	x	—	—	x
1909	Rhode Island	x	x	—	x
1912	South Carolina	x	—	—	x
1903	South Dakota	x	x	—	x
1917	Tennessee	x	x	—	x
1907	Utah	x	x	—	x
1906	Vermont	x	x	—	x
1904	Virginia	x	—	—	x
1915	Washington	x	x	—	x
1916	West Virginia	x	x	x	x
1915	Wisconsin	x	x	—	x
1910	Wyoming	x	x	x	x

Where no "x" is shown, no provision is contained in the law.

In certain States, cases have arisen where pollution by certain industries has caused especial injury to certain streams, and special restrictive legislation applies to these cases.

It is almost a necessary detail, now imposed upon any manufacturer considering the building of an industrial plant, to look into the law regarding pollution in the State or locality he has selected for his plant. In some instances, expense and trouble could be saved by this foreknowledge. For example, in the case of a manufacturer whose waste is especially obnoxious in a certain locality, due to its toxic effect, or destructive action on fish or vegetable life, and the treatment of this to a harmless degree would entail a heavy charge on his operations, he might, by locating in some other place equally advantageous from a business standpoint, escape all or most of the treatment expense.

It is becoming more and more a principle of business economics, to give thought to the waste disposal problem as one of the basic features of plant construction, and to have the necessary plant, for treatment, ready before the factory turns a wheel. Several of the largest concerns in the United States have adopted this policy, thus testifying to the farsightedness of their officials and indicating the increasing recognition of the need for waste treatment.

How far should a manufacturer go in providing treatment? It is obviously a financial hardship to compel or allow a manufacturer to carry treatment beyond the degree necessary to meet the demands of the case. Complete and full spirited cooperation between the health authorities and the manufacturer will prevent such unnecessary expenses, and will tend to a better understanding on both sides. The health authorities should make it part of their duty to inform the manufacturer how far he need go, and endeavor, as far as possible, to help him find the way. This will mean better results and quicker action.

Some wastes, particularly those containing colors in solution, are expensive to treat and require complicated chemical dosings and reactions. Consequently, it is an unnecessary hardship to allow a manufacturer to install a plant that will produce a water white effluent, if less than that will be satisfactory. Recognition should be given to the power of dilution, to eliminate visual nuisance due to discoloration, and the treatment process stopped at the point where this effect is gained. Test work, to provide the necessary type and method of treatment, should always consider

the dilution factor as an essential point in developing the most economical and simple process.

The wise course to pursue is to plan to devise a method that will meet the extreme condition and to construct a plant that will possess flexibility by use of individual units. The worst condition in pollution is usually in the summer seasons, when stream flows are low. At this period, the greatest degree of treatment is required. When stream flows are higher and the dilution greater, less treatment is required, and, at this time, certain units of an intelligently designed plant may be cut out, thus eliminating some of the cost of operation. Several of the States have recognized this principle, and plainly advise those faced with pollution problems, to make careful study along this line.

In those cases where the deposited solids are the cause of the complaint, and color is immaterial, the engineer advising the manufacturer should recommend that he install efficient units to remove the solids and not attempt to produce a decolorized effluent. Chemical treatment of wastes is expensive, and, if solids can be removed to a satisfactory extent, with their use (as frequently happens), the initial cost and the cost of operation of the plant will be less. Often it is possible, by enlarging the units for the deposit of solids, to eliminate or reduce the amount of chemical treatment. In many cases, the interest charges on the extra initial investment for larger units will be less than the daily cost of chemicals that might be required if smaller units were employed. There are, of course, economical limits to this procedure, but it should be given careful consideration in all problems.

Discussion

Anthony V. Delaporte: Mr. Chairman and gentlemen, I came here to learn this morning what I could about stream pollution and how you handle it. Our problems are few compared with yours. Ontario is still an agricultural province. Our industries, with a few noteworthy exceptions, are located in cities and towns. Their wastes are accepted as part of the municipal sewage. With advent of cheap hydro-electric power and its amazing distribution throughout the province conditions are rapidly changing and the municipal problems of to-day are becoming the problems of the small semi-urban industrialized areas. The supervision of stream pollution is in the hands of the Department of Health. Under the

existing legislation the pollution of streams, used either for domestic water supply, or other purposes is reported upon by the Provincial Board of Health. The Department maintains a laboratory and Experimental Station, and a corps of advisers to the Board of Health Experimental Station, and a corps of advisers to the Board of Health. When any question of stream pollution is brought forward, the Department endeavours to work out a solution for the manufacturer, either in the shop, or in our own laboratory before making any recommendation concerning the matter. In all instances we try to impose the minimum of treatment.

In Ontario there are a number of industries, large pulp and paper mills principally, where the waste is receiving no satisfactory treatment. The banks of one river I have in mind are coated with commercial grades of pulp for a considerable distance. Literally there are thousands of dollars worth of such material discharged into the streams of the province annually. Either the management are agreed that the value of the pulp does not pay for its recovery, or they are unaware of the later practices in recovery of paper stock.

Our principal complaints are due in July and August. We have a group of isolated industries discharging to small streams, and with us the minimum run-off coincides with the period of highest temperature. If the waste being discharged into a small stream requires a large amount of oxygen, it upsets the stream during the hot months and a nuisance results. It is not always the waste itself which creates the nuisance, but the new conditions upset the stream balance, and favor the growth of certain organisms, which in turn cause a very definite nuisance. An example of this is a river receiving the effluent of a large distillery discharging waste into the river. This waste itself was inoffensive, but during low water periods the fungus growth in the river caused a serious nuisance in a city several miles away.

President Reese: Is it up to you to find a solution to these problems?

Mr. Delaporte: In the older legislation it was entirely up to the manufacturer to abate the nuisance. Under the existing legislation the Department may be required to report as to the extent of the nuisance and the degree to which the industry shall treat its waste, and the complainant may on the strength of the findings apply to the Supreme Court for an Enforcement Order. *At the present time the Sanitary Division is recommending to the Department*

the allocating of streams for industrial uses, and I have just reported on one stream as suitable for one manufacturer.

DR. MCKEE: Is that statement applicable regarding the newer paper mills and sulphite mills that you have allocated streams? In other words, that you have protected them from interference in the future.

MR. DELAPORTE: We have not protected any yet, but are permitting them to discharge without treatment. Most of the mills in Northern Ontario discharge into the Hudson Bay watershed, where there is considerable dilution and little population excepting a few Indians, trappers and prospectors.

DR. MCKEE: When you do put a manufacturing plant on a stream, or allocate a stream for manufacturing plants, is that an indefinite or a perpetual license to pollute the stream?

MR. DELAPORTE: No! it means that, in the opinion of the Sanitary Division, (the last authority outside of the courts), the situation is one where reasonable precautions, if taken, will prevent the waste from becoming a nuisance such as would support a successful action.

DR. MCKEE: Have you the right to withdraw that ten or twenty years from now, if it is an injury?

MR. DELAPORTE: Yes! The Board may modify the degree of treatment from time to time as the necessity arises, but there is no danger of mischievous injury to industry, providing the industry is prepared to recognize the authority of the province as to the uses of the particular stream involved.

DR. MCKEE: Perhaps I did not make myself plain. Suppose an industry A, of which there were a dozen manufacturers, but you have coming in now a new industry, and you say, "You can discharge your waste in there." Fifteen years from now you can say to the other twelve, who are manufacturing the products A, "On account of the injury you must take care of your waste at considerable expense," but does that apply to the one to whom you have allocated the stream? Is this allocation going to be an insurance against increased expense in future years?

MR. DELAPORTE: Yes! I offer that the present legislation protects the industries from legal actions in no little degree. Its extent is to protect lower riparian owners from gross negligence in regard to the disposal of industrial wastes. On the other hand it provides for a changing use and character of streams. The Department's

policy is to refrain from participation in any common law action unless some municipalities' sources of domestic water is involved, and there is no other solution. The Government is anxious to cooperate with the manufacturers, and recognizes that arbitrary standards applied indiscriminately do not lend themselves to a permanent solution advantageous to the numerous interests involved.

As I understand it our legislation recognizes a changing use in our streams. In some situations the volume and quality of water and type of introduced waste is such as to make the re-use by lower owners advantageous, if the lower owners be protected by a minimum degree of treatment of a waste discharged higher up. In such a case the manufacturers higher up might be asked to do something not originally contemplated, but in no case would they become the prey of pettifogging litigation.

ELECTROLYTIC CONDUCTIVITY AND HYDROGEN ION CONTROL OF WASTE DISPOSAL

By HENRY C. PARKER

Research Department Leeds & Northrup Co., Philadelphia, Pa.

Read and discussed before the Providence meeting, June 24, 1925

Introduction

The application of hydrogen ion and conductivity measurements to the control of waste disposal is a comparatively new subject. Especially is this true of potentiometric hydrogen ion measurements. The knowledge gained from the field of colloidal chemistry and other theoretical considerations, however, point to this type of control as by far the most logical one. It therefore appears probable that, if practical methods and apparatus for utilizing these measurements can be developed, they will fill an increasingly important public need.

The purpose of this paper is to point out a few of the recent developments and improvements which have been made in the apparatus required for applying these measurements to various industrial problems. These improvements have apparently supplied the means for the practical utilization of this method of control in such problems as waste disposal. An application of these methods and apparatus to the problem of sewage disposal is also described.

Cells and Electrodes

Among the new improvements in the apparatus, required for industrial hydrogen ion measurements, are several new calomel cells which have been described in a recent article.[1] A drawing of one of these cells is shown in Fig. 1 at *C*. The new principle upon which these cells operate is that of having the cell divided into two sections by a porous media or a ground glass plug as shown at *G*. The lower section is formed of a porous cup, *F*, through which the saturated solution of potassium chloride gradually diffuses into the test sample. (The latter is usually introduced from a bleeder at the bottom, *M*, of the electrode vessel and passes

[1] Parker and Dannerth, *J. Ind. Eng. Chem.*, June, 1925.

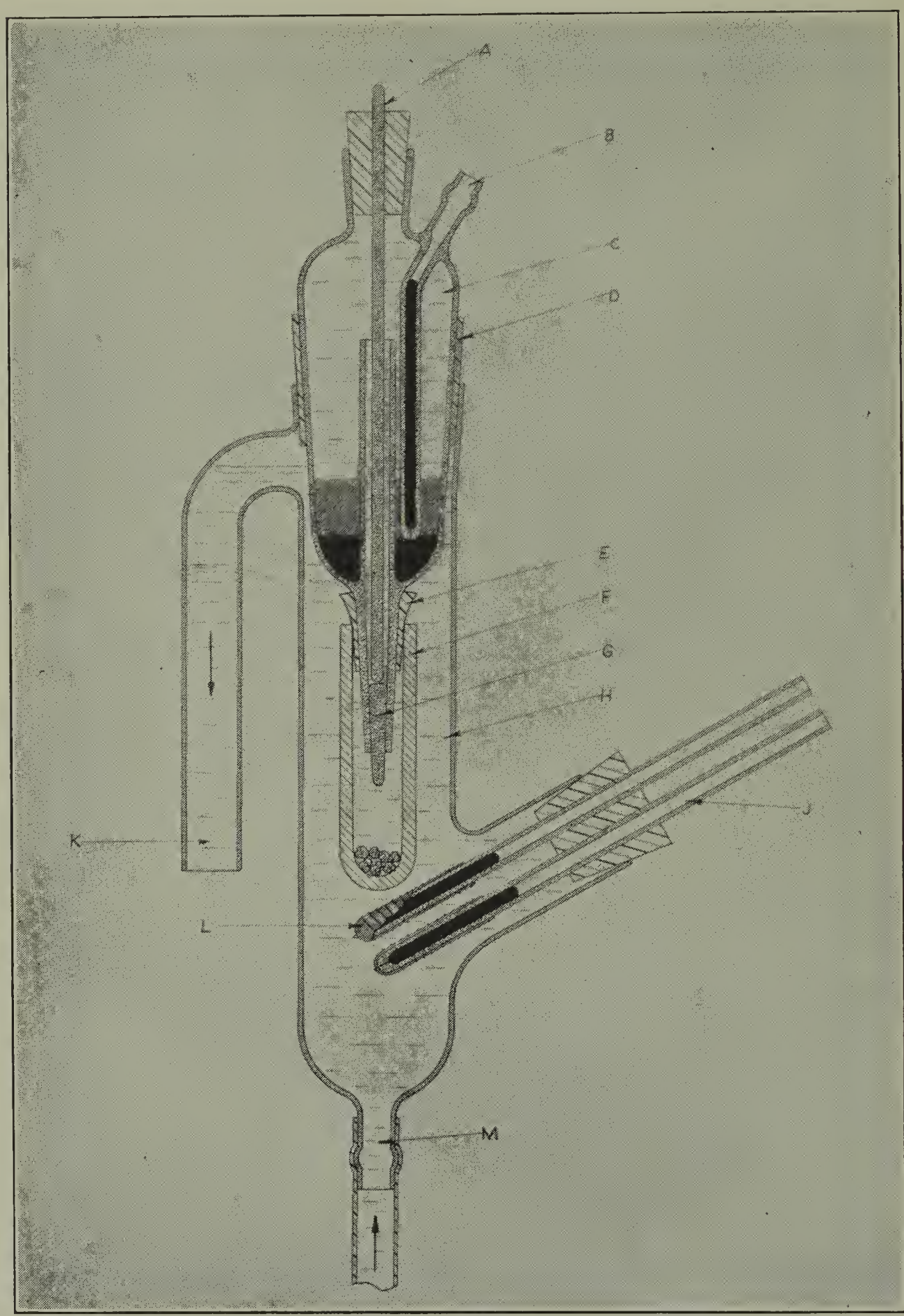

FIG. 1. Flow Type Calomel Cell and Tungsten Electrodes

out the side tube at *K*.) The upper section of the calomel cell contains the calomel, mercury and a solution which is likewise saturated with potassium chloride. The tendency for diffusion past the ground glass plug is very slight and the upper part of the cell is thereby protected from contamination. The extra crystals of potassium chloride placed in the porous cup keep this solution saturated, while the gradual diffusion gives an effect very similar to that of a flowing junction. A calomel cell operating upon this principle requires attention but once a week when additional potassium chloride crystals are added to the porous cup and the upper section is flushed out. When given this attention the cell will operate indefinitely.

The electrodes shown at *L* are likewise a new development and have been described in a recent article.[2] They are constructed by wrapping a fine wire around a thin layer of metallic oxide. These electrodes require no supply of gas, are especially free from the so-called "poisons" which affect the hydrogen electrode and are apparently, by far the best electrode so far developed for a flowing industrial liquor. When used in potable water the electrodes will frequently operate successfully for a month at a time without any attention whatever. In other solutions they require cleaning at intervals, the frequency of which depends upon the amount of suspended solids which collects upon them.

The use of potentiometric measurements before these cells and electrodes were developed was extremely difficult in the case of the great majority of industrial liquors. It is, of course, impossible to use a hydrogen electrode with any accuracy in a flowing solution which is freely exposed to and nearly saturated with air. Other electrodes and calomel cells have required frequent expert attention. These newer developments, however, appear to make measurements feasible in even complex industrial waste liquors.

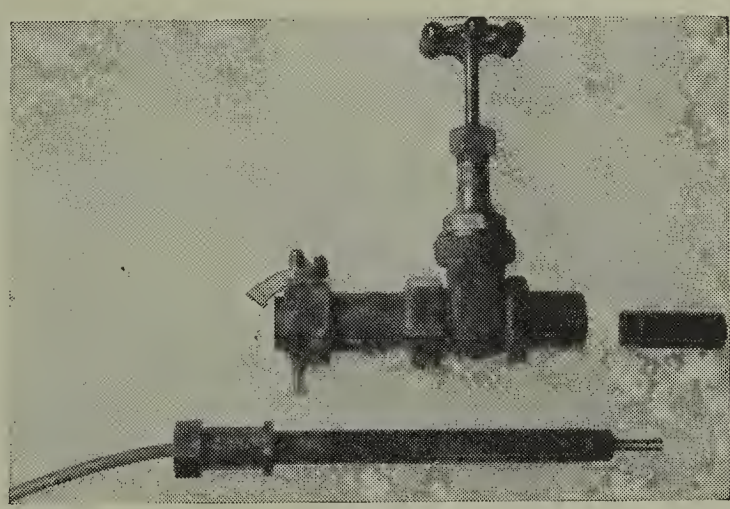

FIG. 2. Removable Conductivity Cell

[2] Parker, *J. Ind. Eng. Chem.*, July, 1925.

Several types of conductivity cells have also been developed which are sufficiently rugged for any industrial use. Fig. 2 shows one of these cells which has been extensively applied for measuring surface condenser leakage. The new feature of this cell is the use of electrodes moulded into an outside metal jacket with bakelite. After many failures, a composition of bakelite was found which would be unaffected by hot water and which would make a joint capable of withstanding 300 pounds pressure without leaking. Use is made of neither packing nor a cement for obtaining a tight seal. The bakelite will withstand neutral or slightly acid solutions but other cells are available which will operate in almost any type of industrial liquor.

Indicating Instruments

A greatly varied line of measuring instruments has been developed within the last few years. For hydrogen ion measurements these are equipped as potentiometers. The same type of instrument, however, when supplied with an A.C. galvanometer and Wheatstone bridge, is then capable of being used for conductivity measurements.

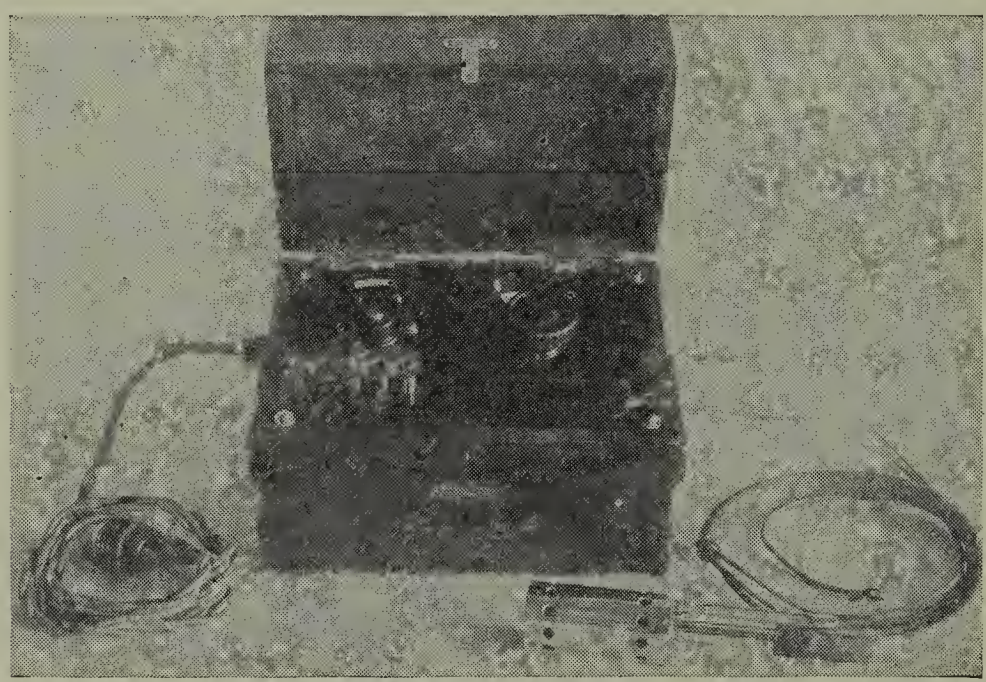

Fig. 3. Portable Conductivity Indicator

The instruments themselves, for the most part, have been developed and used with great commercial success for such varied lines as the hump method of heat treating steel, the measurement of flue gas temperature, the control of furnace temperature, the thermal conductivity method of gas analysis, the measurement of

humidity, the recording of daylight, of turbidity, the recording and controlling of voltage, frequency recording, the recording of soil temperature, of the temperature in a gas calorimeter, of body temperature, of water temperature, etc. The adaptation of the instruments to hydrogen ion and conductivity measurements has been easily accomplished and, while more recent, has likewise met with success.

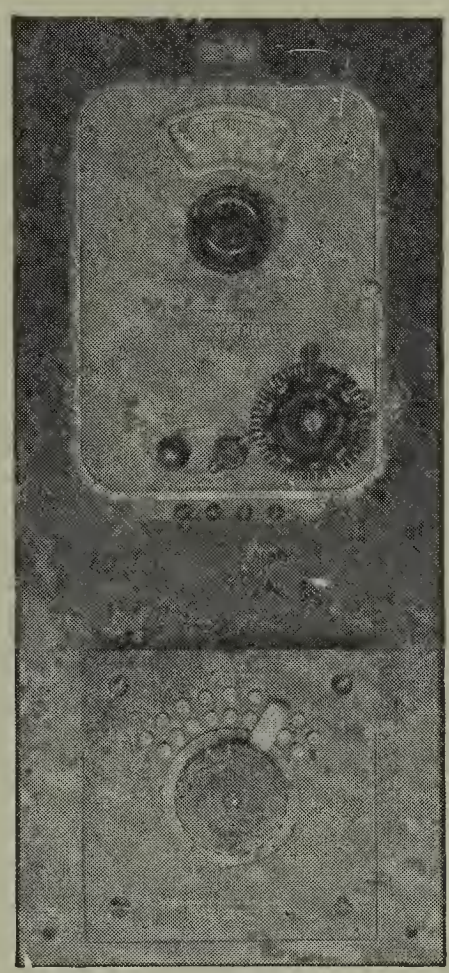

Fig. 4. Wall Type Indicator

In Fig. 3 is shown a portable conductivity indicator which reads, to an accuracy of 1 per cent, resistances between 0.3 and 30,000 ohms and with less accuracy from 0 to 1 megohm. A sixty or twenty-five cycle current is required and an alternating current galvanometer is used. The same type of instrument, fitted as a potentiometer, is available for measuring hydrogen ion concentrations. In this form the instrument has a range from 0 to 1.2 volts and an accuracy of $\pm$ 0.5 millivolts.

In Fig. 4 is shown a wall type indicator with a single range but with a selector switch to throw in any one of a number of conductivity cells. A temperature compensating dial is provided. A hydrogen ion indicator of this same type is also found to be very convenient.

Controlling Instruments

In Fig. 5 is shown a controller especially adapted to conductivity measurements. This instrument may be used to operate signal lights or to control a solution to a definite concentration by opening a valve when the concentration falls too low and closing it when the concentration becomes too high. It may be provided with a temperature compensating dial and a dial to change the concentration at which the control is to operate. This type of instrument is not quite so well adapted to hydrogen ion control, since the instrument in this case would be acting similar to a partial deflector, giving results dependent to some extent on the resistance of the gas chain. Similarly, slight polarization would be caused at the electrodes by the current withdrawn. When this type of instru-

ment is used for controlling a valve the time lag of the system would usually have to be allowed for, either by slowing down the instrument or by throwing the valve in circuit only at infrequent in-

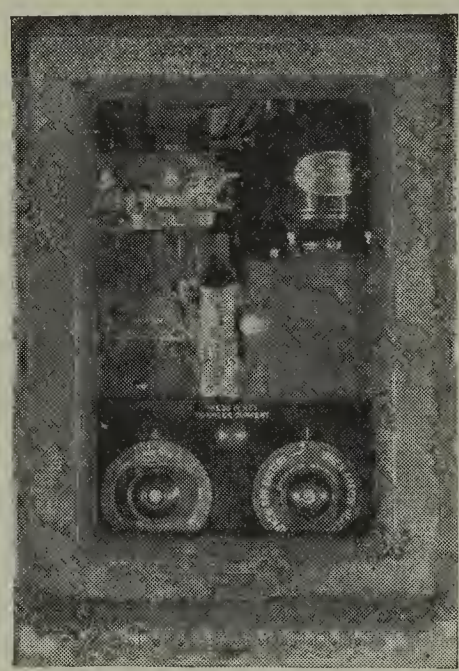

Fig. 5. Controller

Fig. 6. Two Point Controller-Indicator

tervals. A motor operated valve or a system of two differen sized solenoid valves could be conveniently controlled by this instrument.

In Fig. 6 is shown the same type of instrument adapted for use with two or more different conductivity cells. These cells may be operating in solutions of two different concentrations and may be arranged to ring a bell when either solution is above or below a definite range of concentration. A temperature compensating dial is provided for each solution. The scale over which the galvanometer deflects may be used to roughly indicate the concentration in grains per gallon. In the case of this instrument the concentration, at which control is made, can be changed only over a small range of concentration. The same type of instrument may be used for hydrogen ion control within the limitations mentioned in the preceding paragraph. The case of this instrument can be readily water proofed.

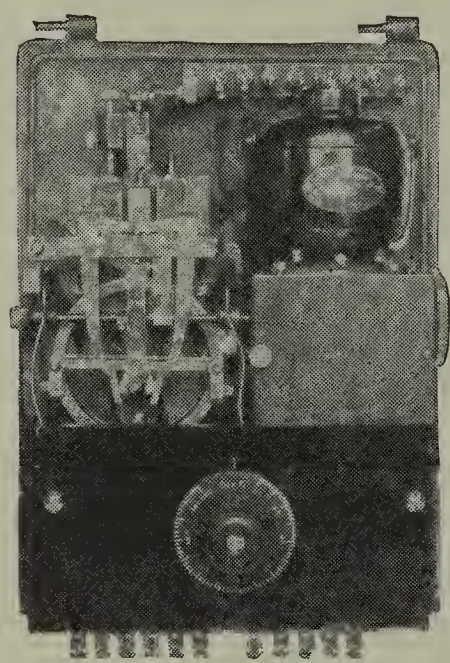

Fig. 7. Proportional Step Controller

In Fig. 7 is shown another controlling instrument which differs

from the preceding in that the control is proportional to the displacement from the required concentration. This is accomplished by having the control operate through the clutch arm and the rotating cams which are seen at the left center of the figure. The clutch arm is tilted in proportion to the throw of the galvanometer and when again balanced by the rotating cams a contact is made whose duration is consequently proportional to the displacement from the control point. The instrument may be provided with a temperature compensating dial and a dial to change the concentration at which control is operated. A potentiometric instrument of this type may be used for hydrogen ion control within the limitations mentioned above. For controlling a valve it is usually necessary to provide gears whereby the speed of the instrument is adjusted to the time lag of the system.

Controlling and Indicating

In Fig. 8 we have a self balancing potentiometer or Wheatstone bridge (according to whether the instrument is fitted for hydrogen ion or conductivity measurements) and we can consequently use this instrument for hydrogen ion measurements with no restrictions whatever. The importance of using a balancing potentiometer rather than a partial deflector for industrial liquors cannot be overestimated. These liquors are sufficiently difficult to measure under the best possible conditions without taking the chance of ruining the measurements by drawing current from the electrodes. This type is also an indicating instrument, the readings being obtained on the upper dial. It can be set to control to a definite hydrogen ion concentration or pH by means of the lower dial. The diagram of connections used in this instrument is shown in Fig. 9.

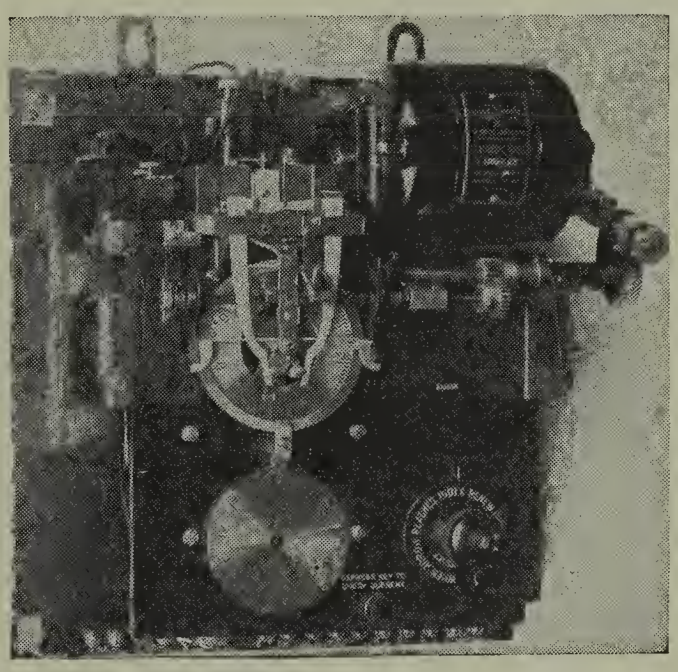

Fig. 8. Proportional Step Controller-Indicator

At intervals, depending on the time lag of the system, the commutator *A* (Fig. 9) is rotated, throwing the sliding contacts,

B and *C* in circuit with the galvanometer. At this time the rotating slide wire will balance to a point corresponding to the setting of the lower dial. During this period the motor operating the valve is in circuit and its motion is proportional to the length of time required for the slide wire to come to balance. When the commutator again rotates, the electrodes are thrown in circuit and the instrument balances at a point corresponding to the pH of the test solution. For a short distance to either side of the control point the motor is out of the circuit.

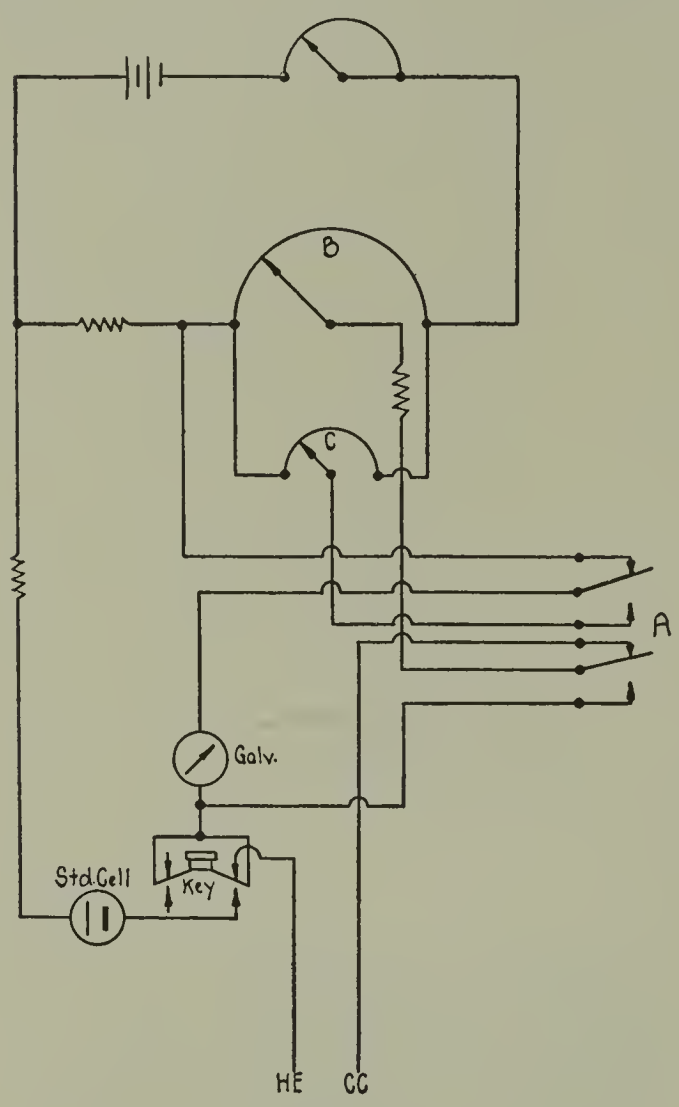

Fig. 9. Connections for H-Ion Controller

The instrument shown in Fig. 8 is, of course, capable of operating as a conductivity controller and indicator. This is accomplished by using an alternating current galvanometer and a somewhat different diagram of connections.

In Fig. 10 is shown a rear view of the recorder mechanism. This instrument is either a self-balancing potentiometer or Wheatstone bridge. It is fitted with control discs, shown in the center, which will operate a signal or valve. The usual manner of using these discs to control a solution to a given pH or a given conductivity is to cause them to operate a solenoid valve on the chemical supply line. A by-pass must be provided which provides not quite sufficient chemicals while the operation of the solenoid valve causes an excess to be added. A second valve can be thrown into the circuit by the instrument if the first is not sufficient to provide an excess of treatment. This method of operation gives a solution of somewhat variable concentration but if an equalizing pond is available, the results are entirely satisfactory.

In Fig. 11 is shown a recently developed per cent conductivity recorder. This may be used to measure the concentration, in

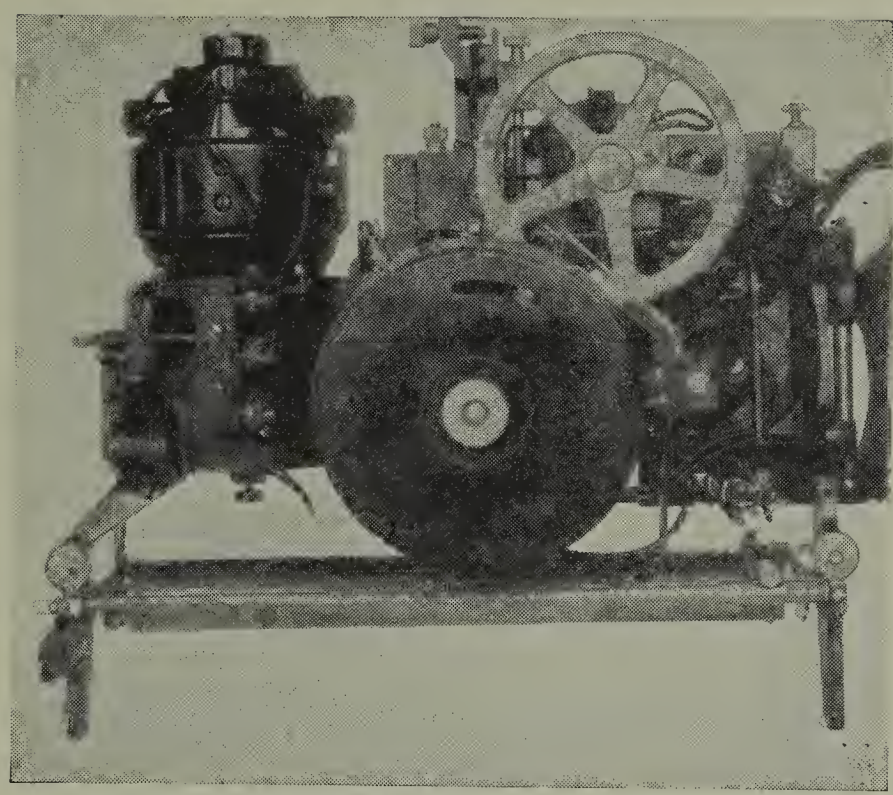

FIG. 10. Rear View of Recorder-Controller

per cent, of a solution which is made from a more concentrated one. The concentrated solution is placed in the cell at the left and, by

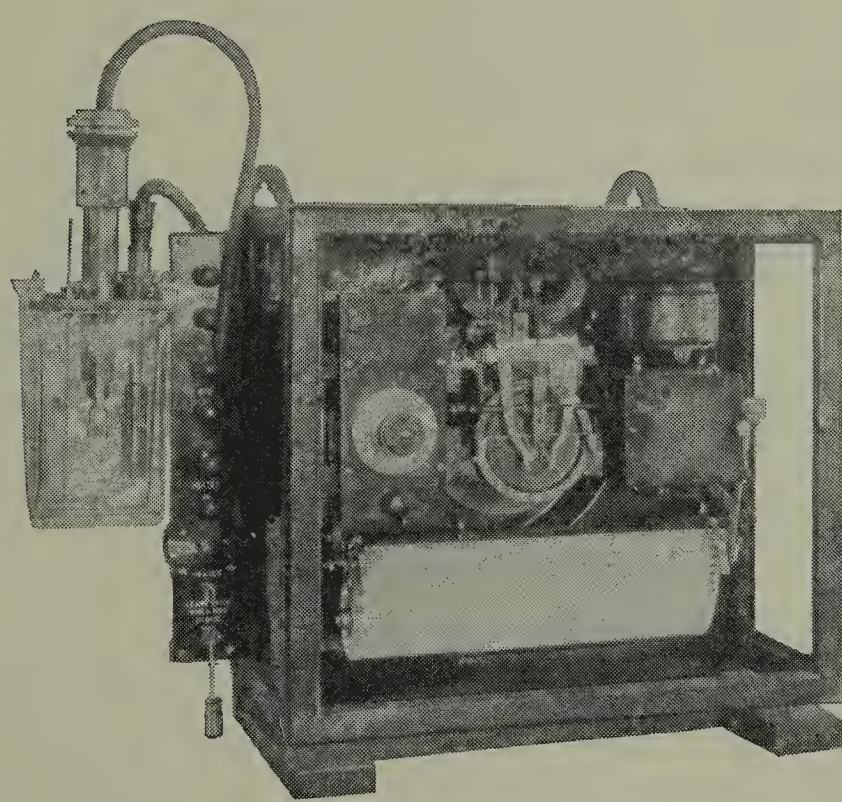

FIG. 11. Per Cent Conductivity Recorder

properly adjusting the temperature and the dial, a reading of grains per gallon of the concentrated solution may be obtained. The recorder gives the per cent of the more dilute solution in terms of

the concentrated solution. If the former is very dilute the scale is almost linear in grains per gallon, since the recorder actually measures values of the specific conductance of the solution.

Finally, in Fig. 12 is shown a self-balancing potentiometer or Wheatstone bridge in which is incorporated the proportional control

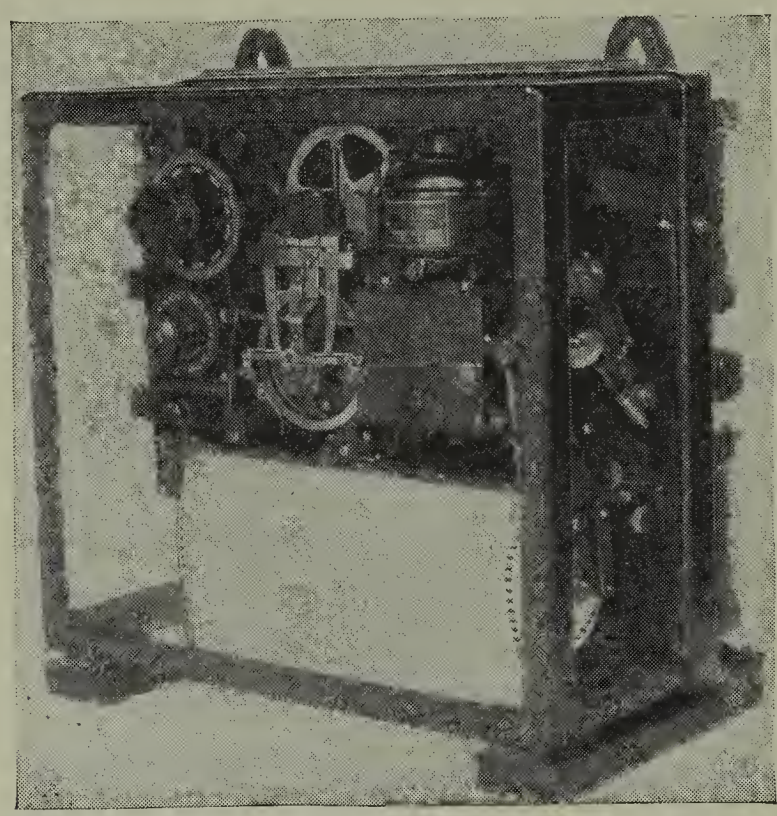

Fig. 12. Proportional Step Controller-Recorder

and a provision for changing the time lag to correspond to that of the system measured. The diagram of connections in this instrument is similar to that in Fig. 9. A dial is provided for setting the control to a given point or a temperature compensating dial may be provided if it is fitted as a conductivity recorder. The mechanism for adjusting the time lag and rotating the commutator is shown at the right.

These instruments may be altered to fit any particular need of a given situation. Several of them are not standard, as yet, for conductivity or hydrogen ion measurements, but it is evident that as soon as the demand for them is created they can readily be standardized. For a conductivity recorder or controller it is necessary to know both the range of resistances (or preferably the specific conductances) over which the measurements are to be made and the temperature coefficient of the resistance. Accurate calibration of such an instrument by means of submitted samples is at times, not entirely satisfactory and it is usually more con-

venient for the operator to do the calibrating in terms to suit himself. A portable indicator can be used to obtain the data required for constructing a suitable recorder. For hydrogen ion measurements it is usually found that the temperature coefficient is so small that compensation is not required.

Aside from the bother of temperature compensation and the preliminary calibration it is usually found that the conductivity method requires less expert attention and is somewhat more "fool proof" than the hydrogen ion measurements. Where an industrial waste has a fairly constant conductivity or where the chemical added for coagulation causes this value to change an appreciable amount, it will probably be found better to apply this method. If a double treatment is used such as in the iron and lime method it might be found advantageous to use conductivity control for the application of the iron and hydrogen ion control for applying the lime.

In any case it is evident from the preceding that instruments are available to meet any situation encountered in industrial hydrogen ion or conductivity control. Conductivity cells and electrodes are likewise available. A wide field is thus opened to chemical engineers to apply these methods to various industrial problems.

Colloidal chemistry teaches us that in the precipitation of such material as is found in the usual trade waste, one or more zones of hydrogen ion concentration usually occur in which the material may be precipitated. The material present usually occurs in colloidal form and its action to change of hydrogen ion concentration suggests that the colloidal particles are capable of adsorbing hydrogen and hydroxyl ions from the solution. In doing so the colloidal particles become charged bodies, the charge depending on the hydrogen ion concentration of the solution. At a certain definite hydrogen ion concentration the particles become electrically neutral and it is in the region of this "isoelectric point" that minimum solubilities, minimum swelling and optimum agglutinations [5] commonly occur. Hence it is frequently found that a trade waste may be sufficiently purified by merely adding chemicals until the neighborhood of the isoelectric point is reached.

In other cases it is first necessary to add chemicals such as alum or iron which themselves form colloids. Later, additional

[5] W. M. Clark, "The Determination of Hydrogen Ions," 2d edition, Williams and Wilkins Co., Baltimore, p. 33.

chemicals are added to precipitate the added colloid and in this precipitation the color and the other colloidal waste material is likewise removed. In some cases it is possible to combine the two methods in that iron or alum is added, thereby altering the hydrogen ion concentration until the solution is in the neighborhood of the mutual isoelectric point. In this case there is a mutual precipitation of the colloids.

While precipitation is taking place only slight changes in either hydrogen ion concentration or conductivity will occur during the addition of chemicals. With hydrogen ion measurements we say the solution is "buffered" while with the conductivity method it is evident that conducting material is being removed from the

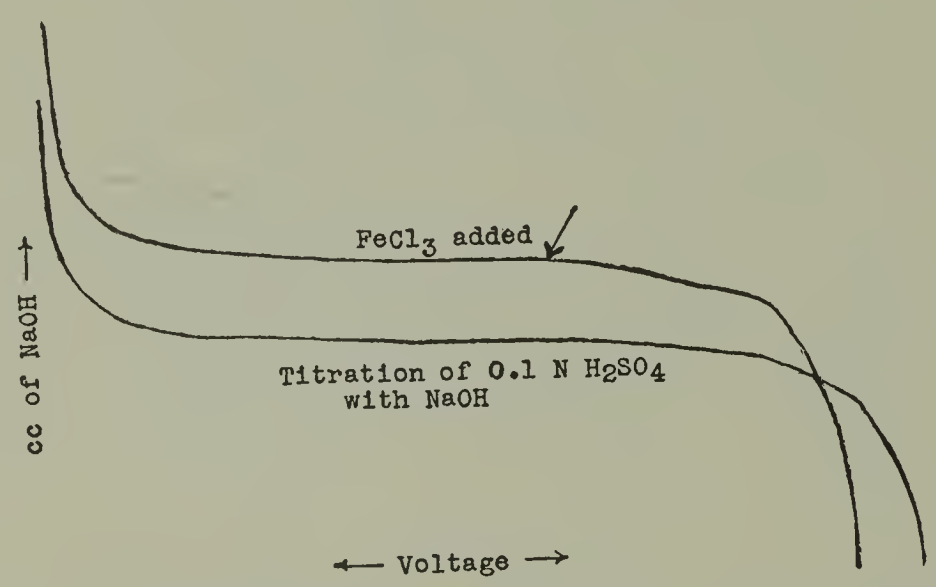

FIG. 13. H-Ion Measurement of Ferric Hydroxide Precipitation

solution (by precipitation) nearly as fast as it is being added. When the material is all precipitated, however, both the hydrogen ion concentration and conductivity change abruptly. Hence if the control is set to operate at a point just beyond complete precipitation it is evident that no appreciable excess will be added before the control stops the addition.

This action is seen in Fig. 13. Two potentiometric titration curves are shown which were made with the instrument shown in Fig. 10 and with one of the electrodes shown in Fig. 1. In the lower curve a 0.1 *N* solution of sodium hydroxide was added from a constant level device to 100 cc. of a 0.05 *N* sulphuric acid solution. The curve obtained is typical of such conditions. It shows a rapid change of voltage in the neutral solutions and a slow change at both ends of the curve. The upper curve was obtained under the same conditions but after the addition of about 0.5 per cent of

ferric chloride to the acid before titration. This solution might represent a typical waste liquor which was being precipitated by the sodium hydroxide. It is evident from the position at the start of the second curve that the ferric chloride acted as a buffer in reducing the acidity of the solution. The ferric hydroxide began to precipitate at the first break in the curve and was apparently completely precipitated in the neighborhood of the arrow. Immediately following this there is a very rapid change of voltage. The arrow is in the neighborhood of pH = 5. It is evident from the shape of the curve, however, that the addition of the precipitating chemical could have been made until the pH was anywhere between 5 and 10 without causing more than a trifling waste of precipitant. This illustrates what economical and excellent results may be expected by the use of this method for control purposes.

If it is necessary to add two chemicals for proper clarification, the second of which precipitates the first, Baylis [6] has found that a minimum of the first chemical is required for clarification at the pH corresponding to the isoelectric point. Wilson, Copeland and Heisig [7] have found that the filtering efficiency of sludge could be increased five times by merely changing the pH to a desired point. In waste disposal methods which rely upon the action of bacteria it has been found that control of pH is important to gain the conditions necessary for maximum growth.[8]

Electrometric control of waste disposal is the only method which will operate successfully under changes of both flow and concentration of the waste liquor. If the precipitation zone is moderately broad, this method will also accommodate moderate changes in the chemical composition of the waste liquor. These facts serve to emphasize the importance if not the necessity of adapting these methods to a practical solution of the waste disposal problem.

The new electrodes shown in Fig. 1 have been applied and found to operate satisfactorily in a variety of industrial solutions. Potable water, boiler feed water, sewage disposal, and waste dye liquors are among the solutions in which they give results which are apparently sufficiently accurate for control purposes.

An experimental installation of automatic control was in operation for some time at Allentown, Pa., in the Direct Oxidation

[6] *J. Am. Water Works Assoc.*, *10* (1923).

[7] *J. Ind. Eng. Chem.*, *15*, 956 (1923); *14*, 128 (1922) and *13*, 406 (1921).

[8] Ref. 4, p. 311.

method of sewage disposal. The application of control to this process was considered one of the most difficult which would ever be encountered. From 30 to 50 parts of caustic alkalinity is maintained for best operating results. The hydrogen ion concentration is thus far over on the insensitive part of the titration curve. Moreover, the lime was added in dry form and this caused the solution, in which the electrode was placed, to be very turbid with undissolved lime which continually deposited on the electrodes. A solution more likely to cause incrustation or deposits of various material on the electrode will probably never be met in practice.

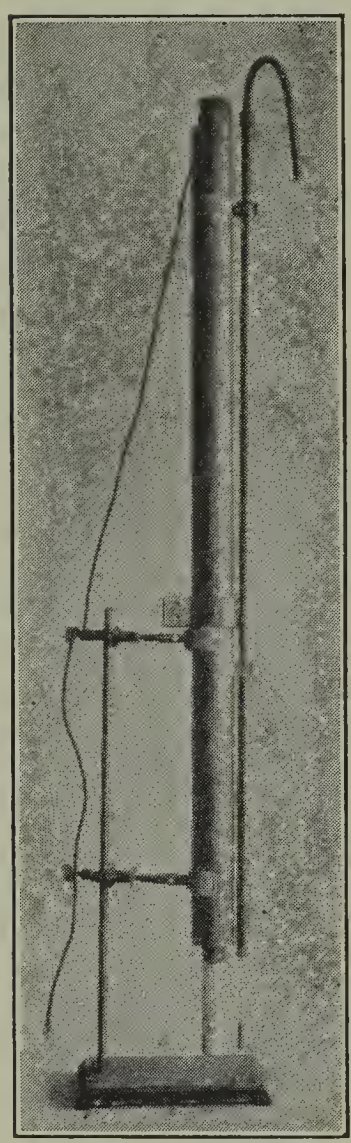

Fig. 14. Calomel Cell and Electrode

In Fig. 14 is shown a photograph of the calomel cell and electrodes which were used in this installation, while Fig. 15 is a photograph of the lime feeding device with the solenoid control attached. The instrument used for recording and control purposes was similar to the one shown in Fig. 10.

In this installation it was found that the electrodes required cleaning every eight to twelve hours. If they were used in rotation the electrodes would last from two to three weeks. Cleaning consisted in brushing off the crust of calcium carbonate in distilled water.

When control of a certain process in chemical industry is made by hand from the results of an occasional titration, it is almost invariably the rule that the general impression is that the desired control is obtained within very narrow limits. When no record is being made of the control it is "anybody's guess" as to just how close to the required concentration a given solution is kept. Frequently the results obtained upon recording the actual concentrations are as surprising as they are illuminating.

Fig. 16 shows the results of hand control at the left and automatic control at the right. The records which were obtained showed that the operators were accustomed to running the plant at average concentrations far below those required for best results. The improvement in quality of the effluent while automatic control was in operation was very striking and it is evident from the figure

that the total variation in alkalinity during this period was one-fourth to one-fifth that obtained by hand operation. The operators found no difficulty in acquiring the requisite skill for handling the electrodes and making up the calomel cells. In fact the satisfactory

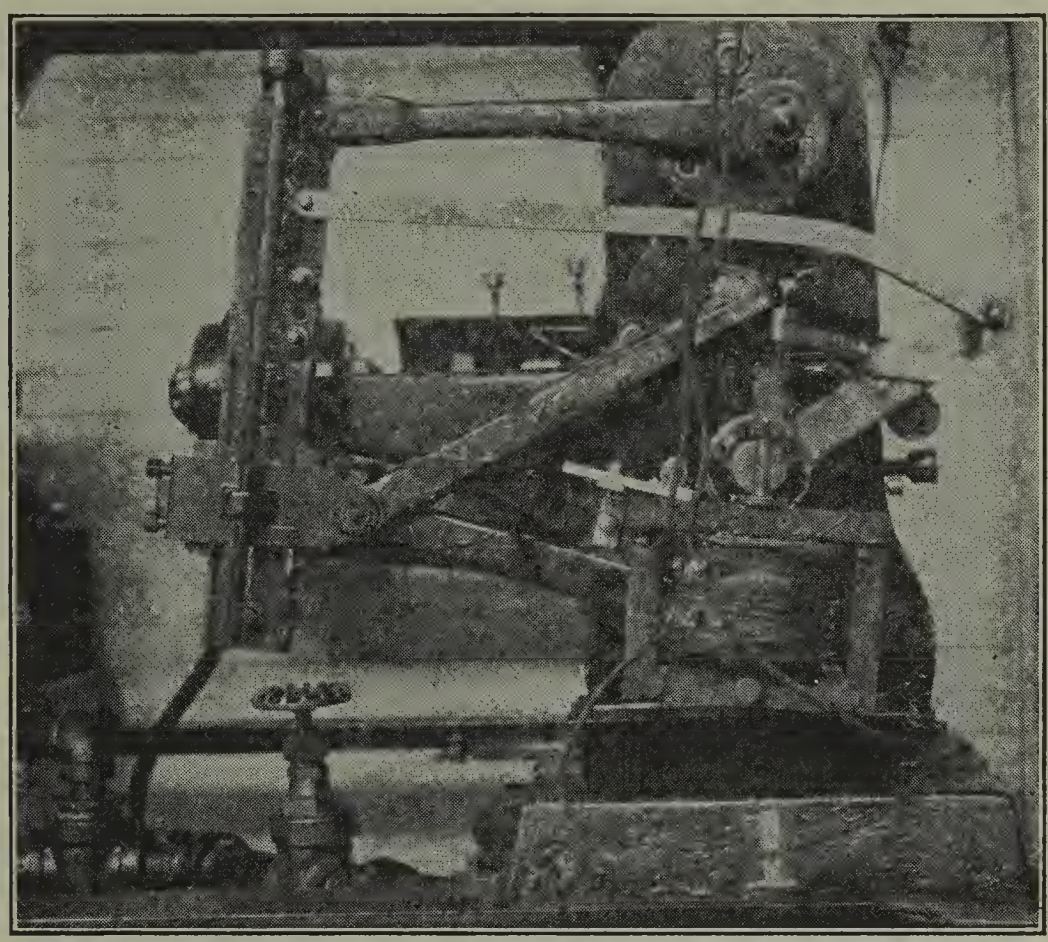

Fig. 15. Automatic Control Attachment for Lime Feeder

results obtained from so difficult an installation would indicate that other waste disposal operations would present but few difficulties.

From theoretical considerations it appears that electrometric control of waste disposal should prove by far the most satisfactory. Recent developments have apparently solved the problem of supplying suitable apparatus for these measurements. There is also available a greatly varied line of indicating, controlling and recording instruments for this purpose. A large field is thus opened for the practical application to various industrial problems. Attention has been called to the apparatus available for these measurements and to the suitability of various instruments for particular problems. The results of the application of hydrogen ion control to the direct oxidation of sewage have been briefly described.

Fig. 16. Hand and Automatic Control of Lime Feed

Discussion

Henry Howard: I would like to ask two questions: First, how Dr. Parker overcame the difficulty of the electrodes fouling in the solution that he spoke of; and, second, what other technical reactions he has controlled?

Mr. Parker: The electrodes were prevented from fouling by washing and brushing them in distilled water. This treatment was necessary every twelve hours but, when given this attention the electrodes would give satisfactory results for two weeks or more.

In reply to the second question, we have used the electrodes for obtaining a record of pH in potable water, in cane sugar juice, in boiler feed water and in waste dye liquors, besides their applica-

tion in sewage disposal. In all of these applications the results appear to be of sufficient accuracy for control purposes.

MR. MURPHY: Dr. Parker referred to the use of the electrodes in boiler feed water. In what way are pH measurements used in this connection?

STUART E. COBURN: Dr. Parker has mentioned the electrolytic method of control. If I may, I would like to say something about the colorimetric method. For about three years we have put that method into operation at a wastes treatment plant, changing the hydrogen ion concentration of the wastes before the application of coagulating chemicals. These wastes have a pH varying from 4.5 to 9.0 and we find by use of brom thymol blue and methyl red we can put a laborer on the job and have him control the pH of the wastes before the addition of the alum, and in that way get excellent coagulation and sedimentation and an effluent of uniform appearance. After alum treatment we use sand filter beds. Formerly, before we put this method into operation, we were not able to filter all the wastes, but now we have never found a time when the beds were not working efficiently. In these wastes, the pH of which varies from 4.5 to 9, we change the pH to 6.4, which we call an optimum, either by the addition of lime or sulphuric acid, and then add the alum solution which results in a final pH of 5.4.

Some of the advantages of this method of pH control have been the reduction in the amount of sludge necessary to handle, the reduction in cost of chemical, the reduction in labor, and the increase in efficiency of the filter beds. Another advantage that we have found in using the colorimetric methods over using electrodes is that we can put a $25 a week man on the job. There is nothing to break and by a few minutes instruction in comparison of colors he is able to carry on this work without difficulty.

MR. MURPHY: Referring to the method for boiler feed control, I would like to inquire in what way he can make use of that in regard to corrosion or prevention of scale formation. I understand that it does not do either.

MR. PARKER: In most power plants an attempt is made to keep the alkalinity of the boilers at a certain value or at least in some definite relation to the scale forming constituents in the boiler water. It is quite generally recognized that such practice not only reduces scale but also corrosion. The electrodes are used in recording the pH of the feed water or in controlling the addition of the

boiler compound in order to keep the feed water at that pH which will give the required alkalinity in the boilers. We have an installation which is recording the pH of the feed water in operation at Perth Amboy, N. J.

Mr. Besselievre: I would like to ask Dr. Parker how pH control accommodates changes in volume or in the flow of the solution?

Mr. Parker: Electrometric control is the only control which will accommodate changes in both the concentration and flow of the influent as well as changes in the concentration of the treating solution. These factors are accommodated incidental to keeping the effluent at a definite pH. If the flow of the influent is doubled it is evident that, in order to keep the pH constant, the control will add double the treating solution. This can be demonstrated by the apparatus we have operating at the A. C. E. M. exhibit. In a closed system we have a small amount of acid being added continuously to a solution. This acid is neutralized by sodium hydroxide whose addition is controlled automatically by a recorder which operates a solenoid valve to keep the solution at a pH of 8.5. Now if we increase the flow of the acid, which would be comparable to changing the flow or concentration of the influent of an open system, the recorder automatically accommodates itself to the change by causing the solenoid valve to remain open over a longer interval. This interval is proportional to the amount the influent is away from a pH of 8.5.

Mr. Parker (communicated): In regard to hydrogen ion control as described by Mr. Colburn, we are always glad to hear of success in the use of colorimetric methods. This method, at best, is intermittent and is entirely dependent upon the "human element." The pH control as obtained by colorimetric methods is so approximate that if this method is successful there can be no doubt that the use of tungsten electrodes will be even more so. Automatic control with electrodes eliminates the "human element," the sampling is continuous, a permanent record of the control is obtained and our experience indicates that the attention required to keep the apparatus in operation approximates fifteen minutes to half an hour per day.

IMPROVEMENT IN THICKENING AND WATER CLARIFICATION

By NOEL CUNNINGHAM

Read and discussed before the Providence meeting, June 24, 1925

In 1907 J. V. N. Dorr developed the automatic continuous thickener. Its invention was in response to the necessity for equipment to compact dilute slime pulps in the cyanide treatment of gold ore and its almost universal adoption has been perhaps the greatest factor in modern hydrometallurgical development. Since its original conception two considerable mechanical improvements have been made, the tray thickener, originated by Mr. Dorr and improved by A. L. Blomfield and what is now known as the super thickener invented by H. S. Coe and perfected by A. L. Blomfield and the operating staff of the Golden Cycle Mining and Reduction Company, Colorado Springs, Colorado.

In spite of its extensive application, the technology of slime thickening has been scanty. In a paper read before the *American Institute of Mining Engineers* at the St. Louis meeting in 1916 H. S. Coe stated the laws governing slime settlement and established the mathematics of thickening.

Wherever essentially non-granular solids are removed from dilute liquid suspension by sedimentation, the settled solids being compacted to a free settled sludge, the operation involved is thickening, and a thickener is a mechanical arrangement for removing the settled sludge separate from the supernatant liquid. Its application can best be illustrated by citing typical examples taken at random.

In ore dressing, hydrometallurgical, and chemical operations, recourse is had to thickening, when scrubber water from limestone crushing and grading is reclaimed for reuse, and to prevent stream polution; when, as in cyanide treatment of ores, classifier overflow at 7 to 1 is to be agitated at 2 to 1, or when a chemical precipitate is recovered from neutralized acid mine water. In industrial plants thickening applies typically where lime mud is to be removed from caustic liquors or where fine pigments are to be collected after

grading by elutriation. In sanitary engineering, thickening has been very successful in its application to sewage disposal plants.

Since its development the thickener has been very effective but it has had the limitation of not being *per se* a finishing machine. Its use with few exceptions has been preparatory to further treatment. Of necessity it has been costly, and recognition in industry of its wastefulness of floor space is indicated by the development of the tray thickener in an effort toward greater compactness.

In 1919 H. S. Coe invented the super thickener to consolidate in one machine a thickener, with greatly increased settling capacity per unit of area and a filter to withdraw emulsified liquid from the free settled sludge. His original idea was of the utmost simplicity, namely to provide a standard thickener with a porous filter bottom; while the sludge was drawn across this filter bottom from the direction of the periphery toward the central outlet it was to be dewatered to the consistency of filter cake by providing a suction under the porous bottom.

Coe submitted his idea to the Golden Cycle staff, a body of men who have worked out more hydrometallurgical problems than perhaps any other. Mechanical difficulties of a very high order had to be overcome and for five years the super thickener has been in constant process of development. During the first three years literally hundreds of arrangements were tried before the machine would function satisfactorily. At the end of this time the major obstacles were overcome and a 30 x 10 ft. machine was constructed which during the last two years has been in constant operation under every possible condition.

The super thickener in its finished form consists essentially of a cylindrical walled tank having a permanent porous false bottom upon which is supported a destructible filter bottom of several feet thickness composed of fine granular particles. Solids in any state of greater or less dilute suspension enter the tank preferably at one side, the flow being across the tank toward an overflow extending around 90° of the periphery. The tank provides sufficient surface area to allow the solids to drop out of suspension, the action of the filter bottom accelerating the settlement of the solids by lowering the density of the column of solids existing in a state of partial suspension. The action of the super thickener filter bottom is as if magnetic particles were passed over a charged magnetic plate, whereas, if the same particles were passed over the same plate un-

magnetized, we would have the comparitive action of an ordinary thickener or settling tank. A slowly revolving single spiral sweep draws the settled solids across the filter bottom from the periphery toward the center of the tank, the continued filter action being sufficient to dewater the settled solids from an emulsion to the consistency of thick, tacky mud, approximating vacuum filter cake. The spiral sweep is lowered an infinitesimal distance at each revolution so that not only the settled compacted solids are removed but also a minute portion of the filter surface, which is thus kept clean and uniformly active.

The application of the super thickener varies according to the solid content of the feed which it is required to handle; as this increases from extremely minute to maximums approaching solid-saturated emulsion the super thickener functions progressively as a clarifier, a thickener-filter and a filter. The range from clarification through thickener-filtering has been so thoroughly studied under all conditions which can be anticipated in practice that presupposing any given condition, the probable super thickener performance can be stated. Within the limits of actual filtration we are not prepared to state as yet what the possibilities of the super thickener are.

Where colloidal content of feed is under 2 per cent or liquid element over 98 per cent the removal of liquid may be entirely through the filter bottom. Flows requiring clarifying vary. Typical instances are; removal of discolorations, as, for instance, vegetable stains from water; elimination of occasional specks of foreign matter from water to be used in the manufacture of high grade paper. With increasing solid content, we encounter undesirable cloudiness due to suspended impurities in liquids for evaporation; cloudiness passes into turbidity of all degrees, the suspended solids often being of such character that settlement and removal by decantation is impossible. As turbidity increases beyond the limit where all liquid may be drawn through the filter bottom, resort must be had to preliminary thickening and removal of the solids, as discussed later, and clarification of turbid or cloudy overflow.

Using the super thickener as a clarifier the spiral sweep is rotated only as required to maintain a predetermined delivery of filtrate. With very small solid content filtration through the granular filter bottom may be actuated simply by gravity but generally a positive pump suction is required. A vacuum pump

may serve but ordinarily sufficient suction is obtained by the use of a force pump adequate for delivering the flow. The caked solids removed by the occasional rotation of the sweep will, of course, be contaminated by the granular element constituting the filter bottom and where this is undesirable or where the advantage of the machine will not more than counter-balance this disadvantage the super thickener does not apply.

The cycle starts with a five-foot-deep granular filter bottom and this is gradually cut away at a rate depending upon the frequency of cut required to maintain flow. With very turbid liquids a cut might be required as often as twice during 24 hours operation, while in many cases a cut might not be required once a month. The amount cut away each revolution of the spiral is controlable but experience has shown 1/100 of an inch adequate; ordinarily the spiral sweep is rotated twice in making a cut so that 50 cuts can be made for each inch of bottom or 3,000 cuts before the bottom must be renewed.

Any granular material is suitable for filter bottom provided it is practically free from colloid. In general the finer the material the better, but where a coarse complex is used it must contain sufficient very fine grains to close voids. Penetration of the filter bottom by the finest colloid occurs only to a depth equal to the diameter of the average particle composing the filter bottom. Theoretically the greater or less coarseness of filter bottom should control the depth of cut in renewing the surface but bottoms varying from quite coarse to very fine have been tried and no difference occurs in results obtained.

As the colloid content of super thickener feed increases above 2 per cent the flow of filtrate falls off sharply and the overflow begins to function. rapidly becoming the chief factor in elimination of excess liquid. With a 3 per cent colloid in feed, the filtrate will approximate normally $1\frac{1}{2}$ tons per ton of dry solid in underflow and as the proportion of solid in feed still further increases with consequent increase of thickness of cake on the filter bottom, the filtrate falls off until on a normal, practically non-permeable ore slime, the filtrate in proportion to dry solid becomes constant at a point slightly in excess of the moisture reduction involved in compacting a free settled slime emulsion to the approximate consistency of vacuum filter cake.

The action of the super thickener thus passes out of the field of

clarification into that of thickener-filtration, the rotation of the spiral sweep is continuous and the products become (1) a comparatively large unclarified overflow, (2) a comparatively small crystal clear filtrate, and (3) a thick underflow approximating filter cake intermixed with a small percentage of granular material composing the filter bottom.

As the proportion of solids in super thickener feed still further increases with proportionate decrease in liquid to be eliminated, the quantity of filtrate, though still maintaining its constant relation to the solid element, begins again to become a considerable element of total liquid product. As slime feed more nearly approaches the consistency of maximum free settled emulsion, overflow practically ceases and action of super thickener leaves the field of thickener-filtration entering that of straight filtration. Work to date in this field has given very interesting indications but has not progressed sufficiently to warrant a discussion at this time.

The actual cost of renewal of granular filter bottom in super thickener operation is so dependent upon local considerations that no general statement on this point is possible. As a basis for comparison elsewhere the following data from the Golden Cycle practice will be of interest.

Thickening-Filtration

Size of Tank, 30 ft. diameter by 10 ft. deep.
Depth of destructible filter bottom, 5 ft.
Tons of destructible filter bottom, 175.
Cost of labor and power renewing filter bottom, $4.00.
Power and labor cost installing each ton of filter bottom, $2\frac{1}{4}$ cts.
Tons of dry slime super-thickened per 24 hours, 200.
Filter bottom cut away per 24 hours operation, $\frac{5}{8}$ in.
Corresponding weight of bottom cut, 4,640 lbs.
Power and labor cost of bottom cut per 24 hours, $5\frac{1}{4}$ cts.
Power and labor cost of bottom per ton of slime super-thickened, 0.026 ct.

Clarification

Filter bottom cut per 10,000 tons solution clarified, 0.5 in.
Filter bottom cut per million gallons solution clarified, 0.2 in.
Filter bottom cut per 10,000 tons solution clarified, 2,900 lbs.

Filter bottom cut per million gallons solution clarified, 1,160 lbs.
Power and labor cost per 10,000 tons solution clarified, 3.26 cts.
Power and labor cost per million gallons solution clarified, 1.3 cts.

At Golden Cycle all conditions for filter bottom renewal are ideal. Sand going to leaching plant is classified on the floor above the super thickener and can be by-passed to flow by gravity into the tank. Bottom renewals occur at intervals which can be anticipated exactly and all preparations made. Preparatory to renewing the bottom the tank is emptied and inspected, any small repairs necessary being made.

The actual placing of the new filter bottom requires about 3 hours and the attention of one man; the sweep is rotated during filling to level the sand coming to the tank and this requires about one horsepower. Where it is necessary to deliver granular material from a remote point in the operation a sand pump will be required. If it becomes necessary to classify a granular element from a plant product carrying a certain proportion of suitable element it involves the use of some simple form of classifier as well as a pump, and it might be necessary to store bottom material to assure quick renewal. If nothing about an operation is available which can be utilized as filter bottom it may be feasible to purchase and store some suitable material. These are all considerations bearing upon cost of bottom renewal, but as this is practically the entire operating cost it is seldom that it will be a formidable item where clarification, thickening and filtration are essential operating features.

In many cases where it is necessary to intermix two elements, as where kieselguhr must be mixed with a gummy colloid to effect filtration, a very exact and intimate mixture is made possible by making the filter bottom one of the elements. This perfect mixing emphasises a very attractive feature of the super thickener; any operator experienced in thickening and filtration knows the trouble and expense involved where elements of varying settling characteristics must be handled simultaneously. In this case the result has invariably been segregation. This applies not only where two elements in the same bath vary in specific gravity, but also where materials of the same chemical composition vary in fineness—the quick settling particles will segregate from those of slower settling rate, a condition which leads to poor washing, loss in filtration, excess liquor for evaporation and non-uniformity of product. The action in the super thickener is to eliminate segregation during

treatment and underflow from the super thickener is too thick to allow segregation in transfer, storage or further treatment.

The super thickener not only provides a new machine for handling old problems to better advantage but makes possible the solution of many problems to meet which there has heretofore been no adequate equipment. It is particularly applicable to dilute suspensions of difficulty settling or gummy colloids.

Discussion

Anthony V. DeLaporte: Mr. Chairman and gentlemen, I have not had a chance to study this paper and I did not know I was coming here until two days ago, and have been motoring ever since, so that I have not had a chance to prepare for any discussion.

One thing I did notice in this paper was the statement regarding the removal of color. I have had no experience with the Super Thickener, but I have had some experience with colors. If you take a line from Georgian Bay to the conjunction of the Ottawa and St. Lawrence Rivers, practically all surface waters north of that line are colored; the colors ranging from 20 parts per million to 500 parts per million on the standard color scale. The question of the removal of the color is of some consequence. We have endeavored to remove the color by various means. We have found that the only way we can get that color out of the water is by the use of alum. The P_H value of the water and the question of color comes back to the question of the amount of alum that we put in. We have had no material success in removing color by filtration alone. In "removing color" I must differentiate. We have two colors, one an apparent color, the other a true color. The apparent color, caused by suspended matter, we can take out by straight sand filters, but when we get to the true color we have to resort to chemicals to overcome it. Up to date we have had no success in removing it in any other way.

A Member: Do you not have to put in something besides alum?

Mr. DeLaporte: We find that we can operate down to a P_H value of 4.5 and get satisfactory results, but we have to rectify the acid condition afterwards, generally with soda ash.

Dr. Withrow: Could they not use lime in that case?

Mr. DeLaporte: We use soda ash instead of lime because we get into other troubles if we do not.

Dr. Withrow: I would like to ask Mr. DeLaporte with reference to the Muskeg waters in the north of Ontario.

Mr. DeLaporte: It was with some of these rivers that we were working.

Mr. Cunningham: We have in one place clarified the water by five foot sand filters, and have had experience at Nighthawk Lake with sand filtration.

Mr. DeLaporte: That is really an apparent color and not a true color.

Mr. Cunningham: Yes, it is an apparent color and not a true color.

Mr. DeLaporte: The apparent color can be removed by filtration but not the real color.

Mr. Cunningham: I was speaking of apparent color, and I thought I ought to say by way of comment that I have referred to the apparent color due to fine infiltration.

President Reese: I suppose what you mean by apparent color is soluble color?

Mr. DeLaporte: Yes.

Dr. R. B. Moore: How many types of material was that experiment tried on?

Mr. Cunningham: That covers all kinds that they can anticipate. That point should have been made more clear. We have been speaking of a specific operation, operated under specific conditions for five years, and intensively for five years.

Mr. Donald B. Bradner: I would like to ask Mr. Cunningham if there is any unexpected factor coming in unexpectedly. That is, two materials, one of which will settle before the second, one on a small scale that if put on a large scale would not settle as well? In other words, can you accurately predict large scale operations from small scale operations?

Mr. Cunningham: There are several members of the Dorr Company present and they have done a lot of work along the lines of correlating large scale operations from small scale tests. In a general way I would say yes that it can be predicted very well from small scale tests, but others here can better state the correlation.

Mr. H. N. Spicer: This is a subject that would take considerable time to explain and on which we have worked for about 15 years. On an average material there is no doubt that the size of large settling units can be determined from small scale tests. We have worked out a test method whereby a unit area is determined for a given flow of pulp under given circumstances, which is used as a basis for the calculations of the total settling area needed.

I am under the impression, however, that Mr. Bradner was asking more than regarding the correlation of small scale tests and practical operation.

MR. BRADNER: I was asking if there were any exceptions or if you had found an exception.

MR. SPICER: If you are sure of getting a really true sample, which is naturally of extreme importance, there should be no exceptions.

In working up the design of a plant to handle a certain product, our laboratory receives samples on which settling tests are to be made. On the basis of these we can determine very closely the size and type of settling unit that should be used.

The big difficulty to be guarded against is that when a new operation is planned, the only way a sample can be had on which to make tests is to prepare one in the laboratory.

The trouble in such cases is that it is extremely hard to make up a pulp which is truly representative and in some cases to make sufficient quantity so that complete settling tests can be run.

Another factor that has to be watched carefully is that a sample taken in an operating plant or a specially prepared one may change before it reaches the laboratory where the settling tests are to be made. We have had some very marked examples of this. The alternative is to send a trained man to the plant to make tests on the spot.

MR. DOWNES: Mr. Spicer has pointed out the importance of securing a truly representative sample.

The usual method of removing sludge from a thickener tank is by means of a diaphragm pump, primarily on account of the control this type of pump gives and its ability to handle heavy sludges. The majority of materials will settle to about as dense as can be pumped.

I would like to ask Mr. Cunningham whether any better means of removing the sludge from the sand filter has been devised.

You point out the value of getting a very dense sludge from your sand filter when it is used in sedimentation operations and you state that the diaphragm pump will remove the settled material as it is discharged.

Do you figure that the majority of sludges settle by sedimentation to a density that is about the maximum at which they can be pumped? I would like to inquire if you have devised any mechan-

ical means of handling the very dense product that you figure to obtain from the sand filter.

MR. CUNNINGHAM: I will give you specific illustrations. If in test work a pulp will settle to approximately 50 per cent solids, in an actual thickener tank you will in practice get a discharge of from 45 per cent to 50 per cent solids.

The sand filter will deliver a product as dense as 67 per cent to 68 per cent solids and a diaphragm pump will handle a pulp as dense as 72 per cent solids.

The sand filter will give a discharge containing about 10 per cent more solids than can be obtained by straight settling.

I have pumped sludge containing 85 per cent solids.

MR. SPICER: From all this I understand that you have handled continuously in a diaphragm pump a pulp containing as low as 15 per cent moisture?

MR. CUNNINGHAM: Yes.

WOOL-SCOURING WASTE LIQUORS, COMPOSITION AND DISPOSAL

By F. P. VEITCH and LEON C. BENEDICT

Read and discussed before Providence meeting, June 24, 1925

The disposal of wool-scouring waste liquors is one of the most important and difficult problems with which industry and chemical engineers are confronted. Wool-scouring waste liquors are exceptionally complex. They contain natural wool fats and waxes, animal exudations and excrement, and large quantities of dirt, loaded with bacteria, to which are added soaps and alkalies, the whole making an emulsion that is exceedingly difficult to break in any practical way and that soon clogs and puts out of commission any known purifying filtering system. On the basis of the figures obtained in the work outlined in this paper, it is estimated that the wool-scouring waste liquors of this country contain from sixty to seventy million pounds of grease, sixty to ninety million pounds of dirt, forty to forty-eight million pounds of potash salts, expressed as potassium sulfate, and fifteen million pounds of nitrogenous matter, expressed as dried albumen. In marketable form these would be worth approximately $5,000,000.

Without question, the object of any wool-scouring plant is to produce a thoroughly cleansed and high-quality product at the lowest cost. During the early years of wool scouring the waste liquors received but little attention, if any, and were emptied directly into the streams, regardless of their polluting effect on the water supply. As it comes from the scouring machines the waste liquor is very dirty, greasy and foul smelling, and in the course of a few hours is rapidly decomposed by fermentation, thus liberating the foul, slimy matter contained in it. This in turn is deposited on the bottom and along the banks of the streams. As these streams, either directly or indirectly, supply the drinking water for many of our villages and big cities, it can be readily seen that sooner or later legislation must be passed to prohibit the introduction of such obnoxious matter. In fact, such legislation exists at the present time in a number of the eastern states. The many wool-scouring plants which are not yet subject to these laws, however, turn their waste liquors directly back into streams without giving

them any purification whatsoever. From the sanitary point of view, these liquors are a most objectionable source of pollution to any water supply. From the industrial point of view, such polluted waters are a serious source of annoyance and expense to all plants which have been built farther down the rivers. In fact, many desirable factory sites have been abandoned because of the pollution of the water supply from such industries.

It is generally recognized that streams into which all the waste liquors, either unpurified or partially freed from grease, are allowed to run are so highly polluted that they are not suitable for household use or for many industrial purposes. We shall, therefore, discuss the pollution itself no further, but consider briefly the methods of purification of the waste liquors and the utilization of the wastes. How may such pollution of our water supplies, with the attendant danger to public health and damage to industry, be avoided, and how may these wastes be put to some economic use? We can not, of course, offer a new solution of this problem, which has been studied by many investigators from practically all angles. Our aim is rather to emphasize the significance of what has been done, in the hope that it may promote a more complete and practical study than has yet been made and a more satisfactory consideration of the numerous processes and types of installation which have been developed to meet this need.

Treatment of Waste-Scouring Liquors

Since only a small part of the six to seven hundred million pounds of wool scoured each year in this country is scoured by the solvent process (to be exact, only two mills are using this process), the waste liquors from the soap-water scouring methods present the most serious problem. For many years it has been known that spent scouring liquors contain by-products which, if they could be recovered economically, would be commercially valuable; in fact, a large number of wool-scouring mills have installed plants to recover one or more of these constituents.

The more important of the methods which have been tried with waste-scouring liquors are: (1) The "acid-cracking" process, one of the first to be employed and still widely used both here and in Europe; (2) the "battage" process (French patent No. 413,442); (3) the treatment of waste liquors with gases, such as sulfurous-acid gas; (4) the steeping process for the concentration of potash,

followed by the acid treatment for grease recovery; (5) the Cardem process, in which, after the grease is removed, the waste liquor is reduced to a dense liquid or to a powder by spraying it into a heated chamber; (6) solvent extraction of grease, followed by potash recovery; (7) the evaporation of the liquors to a small volume and subsequent centrifuging to recover the grease; (8) the clarification of the liquors by centrifuging and the re-use of the centrifuge liquor for scouring more raw wool, thus increasing its potash concentration; (9) centrifuging the settled, heated waste liquors for the recovery of the greater part of the grease, which is of a much higher grade than "degras," and running to waste the partly degreased waste liquor. Of these, Nos. 1, 4, 5, 7, and 9 seem most useful or have been widely used. None of the others will be considered here.

The acid-cracking process has been most generally used, owing no doubt to the fact that its installation does not require a large outlay of money and it can be operated fairly successfully with unskilled labor. The process consists chiefly in treating the waste liquors with sulfuric acid until they are slightly acid, then agitating the mixture by means of air blasts, allowing the sludge to settle, removing and running to waste the intermediate acid-water layer, collecting the agglomerated grease and dirt, together with the fatty acids from the soap, and subsequently recovering the fats and grease by treating the sludge in hot filter presses. The recovery of the fats and grease is fairly complete (usually between 95 and 98 per cent). The recovered grease is of a very low grade, however, and is usually marketed under the trade name of "degras." In the acid-cracking process the potash salts and nitrogenous materials are lost, and the resulting acid liquor containing these constituents is difficult to purify further and can not be discharged into streams without seriously polluting them.

The steeping process, followed by the acid treatment for the recovery of the grease, has been used in England, France and Belgium, as well as in the United States. The object of this method is to obtain a *concentrated* potash liquor, from which potash salts can be economically recovered. In view of the fact that the potash salts on the raw wool are largely soluble in cold water, at which temperature the wool grease is but slightly affected, the usual method is to steep the raw wool in cold water, the tanks (commonly two or three) being arranged according to the counter-current

system, so that the liquor moves in one direction and the wool in the opposite direction. When the concentration becomes high enough, the liquor is condensed to approximately one-tenth its original volume in triple effect evaporators, after which it is incinerated in a reverberatory furnace, producing a red-brown coke containing approximately 40 per cent of potassium oxide. This material is used in making fertilizers, especially for tobacco, where potash in the form of the carbonate is often preferred. The partially washed wool is then scoured in the usual manner to remove the residual grease, and the waste liquor is treated for the recovery of the grease by the acid-cracking process.

The steeping process has met with disfavor because it requires expensive special apparatus and, unless the process is continuous, the liquors become foul and practically unworkable long before the desired potash concentration is reached. Furthermore, the nitrogenous material contained in the liquors is destroyed. Before the World War, the largest recovery and purification plant of this type was in Bradford, England. After the United States entered the war a large plant was erected at Lawrence, Mass., for the recovery of potash salts from waste-scouring liquors. In this plant the ordinary waste-scouring liquors from the first and second bowls were heated and passed through high-speed centrifuges. It was stated that this treatment removed approximately 70 per cent of the grease. The partially degreased waste liquor was evaporated, the solids were charred in rotating kilns, leached, and the potash salts recovered. When the price of potash was high, this plant was able to operate at a profit, but directly after the signing of the Armistice it ceased operations, indicating that this method of treatment can not be considered a commercial success when potash sells at its normal price of approximately $40 to $50 per ton for muriate or sulphate.

The solvent-scouring process, known also as the solvent process, consists of first extracting the grease with a volatile solvent (such as commercial naphtha) and then washing the degreased wool with warm water to remove the suint or potash salts. Only two mills in the United States employ this process today. Of the several objections which have been advanced to this process probably the most serious is that the scoured wool looks dead. Among its advantages are lower cost of scouring, easier recovery of potash salts, wool grease of a good grade, and material decrease, if not

complete elimination, of stream pollution. Several patents have been granted on this process, but the methods and apparatus employed differ only slightly. Briefly it is as follows: The keir or extraction tank is filled with wool (approximately 1000 pounds to a charge) while the movable false bottom, which is attached to the hydraulic ram, is at the bottom of the keir. The cover is then securely fastened on the keir, and the solvent is forced through the wool and allowed to remain in contact with it for from 15 to 30 minutes, after which the false bottom is raised and the solvent pressed out and withdrawn through specially arranged pipes. A second and third treatment with solvent now follow, after which the degreased wool is washed once or twice with warm water, removed from the keirs, and transferred to the ordinary soap- and water-scouring machine, where it is given a final *brightening* scour with a very dilute solution of soap, usually less than 0.1 per cent. This treatment removes the suint and dirt and is said to impart a more "lofty" and brighter appearance to the finished product.

The composition of the material at various stages of the commercial solvent scouring process is shown in Table 1.

TABLE 1

COMPOSITION OF SLUDGE AND WASH WATER FROM SOLVENT PROCESS

Determination	Sludge which Settles to the Bottom of the Tank Containing the Gasoline Extract from Raw Wool		Wash Water Obtained by Washing Wool after Gasoline Extraction
	Before Removal of Gasoline	After Removal of Gasoline	
	%	%	%
Total Solids	34.3	21.0	2.1
Ash	19.2	10.6	1.1
K_2O	4.2	2.5	0.6
Total nitrogen	0.7	0.4	0.1
	Calculated to Dry Basis		
Ash	56.00	50.5	50.7
K_2O	12.1	11.8	28.8
Total nitrogen	2.0	1.8	3.2

The raw wool scoured by this process usually contains a small percentage of water, as does also the solvent used. This accounts for the presence of the potash in the gasoline extract. Ordinarily potash salts are insoluble in gasoline, but, owing to their solubility

in water, they are partially removed with the solvent-grease-water solution.

Smith-Leach Process.—The scouring liquor is evaporated to a small volume, centrifuged to remove grease, and subsequently evaporated and incinerated as described in the "steeping" process. Wilson ("Trade Waste Waters") states that from 55,000 gallons of raw scouring liquor 2 tons of wool grease and 1 ton of potassium carbonate can be recovered.

Centrifuging the settled, heated waste liquors for the recovery of a high-grade wool grease is a process that was developed rapidly in this country during the World War and, with the acid-cracking process, is the one most generally used here. The spent scouring liquors are first run into settling tanks for the removal of heavy materials, such as sand and dirt, and then through heating coils into high-speed centrifuges, where a large portion of the wool grease is removed. The resulting liquor, although containing considerable grease and other impurities (largely nitrogenous) derived from the raw wool, is emptied directly into the streams. The recovered grease is of fair quality and finds extensive uses in the manufacture of cosmetics and many other articles. However, this process falls far short of needed effectiveness both in purification of the liquors and in the recovery of their components.

Experimental Work by the Bureau of Chemistry

Search of the literature showed that the information on the composition of the impurities present on raw wool of various types and grades and on the quantities of such impurities and also on the composition of the waste liquors in which known wools had been scoured was fragmentary and unsatisfactory. For this reason we undertook the analysis of a large number of wools, endeavoring to have a sufficient number of samples of each type to establish with reasonable certainty the maximum, minimum and average percentages of the more important constituents present in each type. On some types we fell somewhat short of our aim.

Whenever possible, a member of the Bureau selected the samples, thus making sure that they were reasonably representative of the raw wool or the waste scouring liquor, as the case might be. These samples were shipped immediately to Washington, where they were carefully subsampled before analysis. The plan of procedure for raw wools was as follows: Moisture was determined at 100–105° C.

TABLE 2

IMPURITIES IN WOOL OF VARIOUS KINDS

(Based on Wool as Analyzed)

Grade	Number of Samples	Moisture	Pet. Spirit Extract			Total Ash			Water Extract			K_2O in Water Extract			Nitrogen in Water Extract
			Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	
		%	%	%	%	%	%	%	%	%	%	%	%	%	%
Fines	93	5.6	41.9	17.4	6.1	47.6	23.8	8.7	22.9	14.0	6.3	6.5	3.6	1.1	0.51
½ Blood	48	5.5	27.7	12.7	5.9	36.8	23.0	10.0	22.6	15.2	10.6	5.7	3.9	2.0	0.57
Medium	29	5.0	16.6	10.5	5.5	46.8	19.0	8.9	27.4	14.7	8.8	7.0	3.6	1.3	0.48
⅜ Blood	44	6.3	16.3	9.8	6.7	38.0	19.4	9.7	33.0	16.8	8.1	5.9	4.5	1.9	0.60
¼ Blood	38	7.0	15.0	8.6	6.4	34.5	18.3	9.7	25.7	15.4	6.1	7.3	3.9	1.4	0.52
S. Amer. Mis.	14	6.2	15.1	11.3	7.6	42.1	23.1	8.9	22.3	13.8	7.2	5.9	3.5	1.3	0.27
Miscell.	29	6.4	23.9	12.8	5.7	35.1	22.8	5.9	19.8	14.8	3.6	5.9	3.8	0.2	0.54
Pulled	10	3.5	19.4	10.8	5.1	19.8	8.9	3.7	5.1	3.5	1.7	0.7	0.2	0.1	0.31
Total	305	5.87	—	12.87	—	—	21.22	—	—	14.55	—	—	3.77	—	0.52

The sample was then completely degreased in a Soxhlet extractor, using petroleum spirit as the solvent, the resulting solvent-grease solution was evaporated, and the residual grease was determined. The degreased sample was extracted in the same apparatus with boiling distilled water and the water extract was taken to dryness, thus giving the total water-soluble extract. This residue from the water extract was again dissolved in distilled water and made to known volume. An aliquot was evaporated to dryness and finally ashed to constant weight, thereby affording a means of ascertaining the relative percentages of organic and inorganic matter which had been extracted by the distilled water treatment. The potash (K_2O) content of the water extract was then estimated on another aliquot, according to the methods of the Association of Official Agricultural Chemists for fertilizers. A third aliquot portion of the water extract was used for the determination of the nitrogen content by the regular Kjeldahl method. Finally the total crude ash content of the raw wool was estimated on a thoroughly dried sample of the original raw wool by burning to constant weight in an electric muffle.

TABLE 3

MEAN GREASE AND POTASH CONTENT OF RAW WOOLS BY LOCALITY

Locality	Number of Samples	Pet. Spirit Extract	K_2O in Water Extract
		%	%
United States	213	12.74	3.98
South America	33	10.36	3.42
Cape	20	16.14	3.90
United States (pulled wool)	10	10.83	0.24
Australia and New Zealand	22	15.50	3.19
Miscellaneous	7	13.15	4.20
	305	12.85	3.80

Tables 2 and 3 show the maximum, minimum, and average results of analysis of some similar 305 samples of various wools in the grease. A careful examination of these figures should afford information directly applicable to the problem of treating waste-scouring liquors. Speaking broadly, the average wools being scoured in this country will probably yield 13 per cent of grease, 4 per cent of potash (K_2O), $\frac{1}{2}$ per cent of nitrogen, 21 per cent of ash, and $14\frac{1}{2}$ per cent of water-soluble matter of which about 3 per cent is nitrogenous matter. These averages, however, can be used

only in a general way. Should data on the individual wools of any one type or grade be desired, reference should be made to the results published elsewhere. It is important to note that the average figures for the water-soluble potash content of wool of different kinds or of wools from different countries do not differ widely, except, of course, in the case of pulled wools, although the grease content may differ materially with the kind of wool being scoured.

No attempt has been made in the tables to effect more than a general classification of wools. The data on individual samples will be published later. The wide variation in grease and water-soluble potash content of different samples of the same kinds of wool, however, is interesting, especially as both are to a large extent governed by genetic and geographical conditions. For example, the sample of fine wool, which contained approximately 42 per cent of grease, was grown in Ohio under ideal genetic and grazing conditions and was practically free from dirt and sand, whereas the sample containing only 6 per cent of grease was grown in Texas, where the sod was so scanty that the fleeces were heavily contaminated with fine red sand and vegetable matter. The per cent shrinkage of these two samples was approximately the same, but it is obvious that they would require different handling in scouring and their waste-scouring liquors would differ materially in composition. This is mentioned merely to bring out the exceedingly wide variation which may be found in wools of the same grade.

Wool Grease

As is well known, the most objectionable, and from an industrial point of view the most detrimental, constituents of waste scouring liquors are the wool grease and decomposed soaps. Wool grease is an exudation from the body of the sheep, which serves the purpose of a protective coating from the wool fiber during its growth. It consists for the most part of higher alcohols and therefore has the properties of a wax rather than those of a true grease. As pointed out by Andes ("Animal Fats and Oils"), crude wool grease is a greasy yellow or brown mass, with an unpleasant smell, containing a large quantity of cholesterin, isocholesterin, stearic, and palmitic-cholesteryl-esters, which make it imperfectly saponifiable by alkalies. For this reason and also because of its insolubility in water, the method employed in removing it from raw wool is one of emulsifi-

cation. The waste liquors, therefore, contain the natural wool grease very closely emulsified with the scouring agents used, as well as with the potash salts present on the raw wool.

Of the numerous methods proposed for the recovery of wool grease, only the following three are used today in this country—the acid-cracking process, the centrifuge process, and the naphtha solvent extraction process. The selection depends to a large extent upon State laws relating to the pollution of streams, the type of wool scoured, and whether "degras" or "neutral wool" grease is to be recovered.

Scouring mills in States which have rather rigid laws governing stream pollution usually employ the acid-cracking method. As recovered by this treatment the grease is a brown-black, greasy mass, with an unpleasant smell, containing true wool grease, fatty acids from decomposed soaps, fatty acids from the original wool grease, inorganic salts, which were either present on the raw wool or were added during the scouring, decomposed albuminous and glutinous matter, and a fraction of one per cent of sulfuric acid.

Some investigators believe that this material can be purified and converted into "lanolin." The Bureau's attempts to do this have been unsuccessful. It appears almost impossible and clearly impracticable to accomplish this purification on a commercial scale. The relatively high temperature employed in the process of pressing out the grease decomposes the albuminous matter, forming exceedingly stable dark colored compounds, which in turn are so closely mingled, if not actually combined with the true wool grease, that the strongest bleaching agents have but a very slight effect upon the grease. The conclusions, therefore, are that more than a partial purification of recovered grease of this type would be very costly and commercially impracticable.

The centrifuge process gives much better and more uniform grease, which with proper treatment can be converted into either "neutral wool grease" or "lanolin." The industry finds that best results are obtained when the waste-scouring liquors, after thorough settling, are heated to approximately 190° F. and conducted directly into high-speed centrifuges, operated under 35 to 40 pounds of steam pressure and at a speed of from 15,000 to 17,000 r.p.m. As it is delivered from these machines the grease is of a medium brown color, has a slight odor of sheep and soap, contains between 4 and 5 per cent of water, and possesses an acid value of from 3.5

to 4. It is the custom in some mills, which scour only high-grade wools, to recentrifuge this grease, which gives a product containing less than 1 per cent of water and having an acid value of from 0.5 to 1. This product finds a ready market with any lanolin manufacturing establishment and is quoted at from $0.04 to $0.07 per pound.

Naturally the composition of the degreased waste liquors coming from the centrifuge varies considerably. Such a liquor from scouring wool showed: Ash, 1.03 per cent; potash (K_2O), 0.81 per cent; grease (as wool grease), 0.08 per cent; fatty acids, 0.82 per cent; nitrogen, 0.08 per cent; and total solids, 2.93 per cent.

Because of its low grease content, such waste liquors can be treated for the recovery of the fatty acids and potash at a decidedly lower cost than can the original liquor carrying the grease. It was observed that the greases recovered from the waste liquors from the better-grade wools were much lighter in color and contained a smaller percentage of free fatty acids and nitrogenous matter, indicating that different recovery methods may be advisable for treating scouring liquors from wools of different types and grades.

The results of our experiments on greases recovered from commercial waste-scouring liquors indicate that the main constituents of such greases are free fatty acids, resulting from the decomposition of the soaps, free fatty acids from the wool fat proper, neutral saponifiable matter, consisting of esters of fatty acids, and unsaponifiable matter, consisting of free alcohols, such as cholesterol and isocholesterol. Purified wool fat may be said to consist mainly of two portions, one, melting at approximately 60° C., which is insoluble in alcohol and also unsaponifiable, and another, melting at approximately 15° C., which is soluble in alcohol and also saponifiable.

Wool grease is used, either in its crude or refined state, in soap manufacture, rubber manufacture, leather manufacture, hoof salves, rust preventatives, improving oils poor in fats, as a substitute for tallow, palm oil and castor oil, mixed with tallow, graphite, etc., for locomotives, in wire drawing oils, wire cutting oils, rope and cordage manufacture, in lanolins, ointments, cosmetics, and shaving creams, and in sticky mixtures for catching insects, lithographic and multographic inks, calico printing inks, shoe blackings, wool oils for carding and combing wools, special varnishes, and quenching oils, for waterproofing and coloring electric bulbs, special cylinder

oils, stop-cock greases, pyroxylin coated fabrics, foam breakers, waterproofing fabrics, etc., and as a lubricant in steel rolling.

The annual production of wool grease in this country has been estimated to be between 40,000 and 50,000 barrels; the consumption averages approximately 70,000 barrels; thus nearly half of the wool grease used here must be imported. The imports for January, February, and March of this year through the ports of Boston, New York, and Baltimore alone amounted to over 3,100 barrels per month. These figures show an urgent need for the development of some economical and adequate method for treating waste-scouring liquors for the twofold purpose of recovering the grease and eliminating one of the most serious sources of stream pollution.

Although waste-scouring liquors contain only about half of one per cent of nitrogen, the nitrogenous matter (not including that which settles out with sand and dirt) is nevertheless one of the important constituents, from both a purification and fertilizer point of view. Several of the larger scouring plants have tried methods of recovery based especially upon the content of potash and nitrogen obtainable in the finished product. In considering the possibility of utilizing waste scouring liquors in fertilizers, the forms in which the nitrogen existed in such liquors were determined. Practically all the nitrogen was present in the forms commonly found in the urine of animals and in the percentages shown in Table 4. This summary, although not complete, furnishes fairly comprehensive information on the more important compounds of nitrogen present in a representative sample of waste scouring liquors and their fertilizer value.

TABLE 4

PARTITION OF NITROGEN OF WASTE WOOL-SCOURING LIQUORS

	% of Total Nitrogen
As Ammonia	2.4
As Urea	18.0
As Hippuric Acid	11.6
As Allantoin	10.9
As Uric Acid	11.8
As Protein	28.8
As Amino Acids	3.1
As Undetermined	13.4

Turning again to the handling of the waste liquors, it appeared that the most promising line of work would be a procedure which

would give a waste liquor containing enough potash salts and nitrogenous matter to make, when evaporated, a fertilizer, recover a neutral wool grease, settle out dirt usable as a fertilizer filler, and yield water for use in boilers and for scouring. We realize, of course, that such a process would necessitate fundamental changes in the wool-scouring process commonly employed, which, we are frank to say, seems neither impracticable nor even undesirable. The demonstration on a commercial scale and the success of the proposed process will depend, of course, on the courageous support of a scourer or group of scourers, who have the means and the patience to work it out practically.

The process which we recommend as most promising, but for which no great claims of originality are made, consists in (1) extracting the grease with naphtha in keirs, as is now done in several large mills, then scouring with soap and water as usual; or (2) as the counter current system, scouring as usual with alkali and soap. In both cases the wash liquor is used until that in the first bowl is sufficiently concentrated to permit economical evaporation, or to about 20 to 25 per cent of total solids, including sand and dirt. In (1) the grease is recovered by distilling off the naphtha under reduced pressure and below 95° C. In (2) the grease is removed with the centrifuge. The first-bowl waste liquor is further concentrated in triple or quadruple effect evaporators to 60 per cent solids and finally dried on a drum to a product containing approximately 5 per cent moisture.

In studying the proposed procedure samples of Australian wools when raw and after they had passed through the second bowl were obtained from several scouring plants. The composition of the matters removable from these wools is shown in Table 5. The results are based on the air-dry wool in the condition as received.

The quantities of wool scoured were as follows: No. 1, 11,973 pounds; No. 2, 10,881 pounds; No. 3, 11,764 pounds; No. 4, 11,800 pounds; No. 5, 10,146 pounds. All the wool was taken from a shipment of Australian 70's. Bowl No. 1 held 800 gallons, and No. 2, 1,000 gallons. "Red-oil potash" soaps were used in the scouring; therefore the liquors are a trifle higher in potash than they would be if sodium soaps had been used.

The figures in Tables 5 and 6 are regrettably inconclusive, as during the washing of each lot of wool both the first bowl and the second bowl were dumped four times each. The figures are en-

couraging, however, in showing that the greater part of each constituent is removed in the first two bowls, and also because laboratory tests indicate that these concentrations may be approached in scouring.

TABLE 5

MATTER REMOVABLE FROM WOOLS IN FIRST AND SECOND BOWLS

Sample	Composition						
	Moisture	Grease	Total Ash	Water Extract	Ash of Water Extract	K_2O in Water Extract	Nitrogen in Water Extract
	%	%	%	%	%	%	%
No. 1: Raw	6.30	17.01	17.80	15.81	6.26	3.47	0.88
End 2d bowl	7.28	3.17	3.06	2.13	0.62	0.23	0.12
No. 2: Raw	7.06	16.80	17.70	7.57	4.22	2.41	0.40
End 2d bowl	6.98	2.85	2.76	2.34	0.67	0.25	0.15
No. 3: Raw	7.96	16.06	16.85	11.08	5.31	2.82	0.40
End 2d bowl	6.74	4.34	3.59	2.84	0.84	0.44	0.18
No. 4: Raw	7.85	17.76	17.74	11.82	5.35	2.50	0.47
End 2d bowl	6.62	4.77	4.06	3.01	0.96	0.32	0.18
No. 5: Raw	7.76	20.33	12.96	10.03	4.52	2.42	0.43
End 2d bowl	7.81	1.59	3.05	3.62	1.26	0.23	0.16

TABLE 6

CONSTITUENTS REMOVED FROM RAW WOOL IN FIRST TWO BOWLS [1]

Sample	Constituents				
	Grease	K_2O	N	H_2O Extract	Ash
	%	%	%	%	%
No. 1	11.0	2.6	0.5	19.3	11.5
No. 2	10.0	1.6	0.2	3.6	10.9
No. 3	15.0	1.9	0.2	6.3	10.0
No. 4	10.2	1.7	0.2	7.3	10.20
No. 5	12.5	1.5	0.2	4.0	6.8

[1] These figures are calculated from the loss from the wools and are stated on the basis of the waste liquors in order to show what would have been the concentration of the waste liquors had it been practicable to scour all the wool of each lot without dumping the bowls.

Within recent years a large scouring plant in New England has conducted extensive large-scale experiments on concentrating its normal waste liquors from the first two bowls. This mill scours only wools of half-blood or higher grades and uses a red-oil potash soap as a scouring agent. As would be expected, its waste liquors were comparatively high in grease and potash.

TABLE 7

COMPOSITION OF WASTE-SCOURING LIQUORS FROM FIRST AND SECOND BOWLS (LIQUORS FROM WOOLS IN TABLE 5)

Sample	Bowl	Total Solids	Pet. Ether Extract	Total Ash	K_2O	Nitrogen	Total Solids in Filtrate	K_2O in Filtrate
		%	%	%	%	%	%	%
No. 1.....	1	5.1	2.2	1.3	0.4	0.12	2.0	0.5
	2	7.5	3.6	1.9	0.7	0.17	2.6	0.7
No. 2.....	1	6.0	2.9	1.5	0.5	0.14	2.3	0.5
	2	7.3	3.3	1.8	0.6	0.16	2.6	0.6
No. 3.....	1	11.0	4.2	3.0	0.9	0.23	3.8	1.0
	2	1.7	0.9	0.4	0.1	0.02	0.8	0.1
No. 4.....	1	10.6	4.7	2.7	0.9	0.22	3.1	0.9
	2	1.8	0.9	0.4	0.1	0.03	0.7	0.1
No. 5.....	1	9.9	5.2	2.6	0.9	0.21	3.7	0.9
	2	1.7	1.9	0.4	0.1	0.03	0.8	0.1

Of all the normal first-bowl liquors examined during this work those listed in Table 7 are the most concentrated. The method employed at the mill in handling these liquors was as follows: As they were removed from the first and second bowls the waste-scouring liquors were conducted first into a settling tank, where a large part of the dirt, sand, and suspended matter settled. The partially purified liquors were then heated and passed through a series of Sharpless centrifuges, which removed approximately 75 per cent of the grease, and then conducted into triple-effect evaporators, from which they emerged as a thick, brown-black, semi-solid mass, containing approximately 60 per cent of total solids, having the following composition: Total fatty matter, 14.2 per cent; volatile fatty acid as acetic, 6.1 per cent; grease soluble in petroleum spirit, 7.2 per cent; nitrogen, 1.2 per cent, ash, 21.7 per cent, moisture, 41.6 per cent; total potash (K_2O), 14.4 per cent; and water-soluble potash (K_2O), 12.7 per cent.

By further drying on a drum to 5 per cent moisture, the product would contain 22 per cent of grease, 1.97 per cent of nitrogen, and 20 per cent of water-soluble potash. The percentage of grease, although high, is not sufficiently high to make the product unsuitable as a fertilizer raw material. The value of the products obtained in this large-scale experiment on evaporating ordinary waste wool-scouring liquors, we are advised, slightly exceeded half the cost of the operations. We are not prepared to say, however, that the complete recovery and utilization of the wastes, the production of a pure soft water for boiler and scouring purposes, and the total elimination of all stream pollution, with the consequent sanitary and industrial advantages, may not justify this expense.

Laboratory Experiments to Obtain a Concentrated Waste Liquor

Additional data on the practicability of obtaining a more concentrated liquor for evaporation and thus greatly reducing the cost of this operation were needed. Accordingly the Bureau of Chemistry undertook a series of small-scale washing experiments, using a naphtha-degreased Vermont fine wool having the composition shown in Table 8.

TABLE 8

Composition of Vermont Fine Wool

	On Raw Wool, per cent	Degreased Wool, per cent
Moisture	2.6	7.1
Grease	16.1	—
Ash	15.3	13.2
Potash (K_2O)	4.8	5.0

Three pounds of the degreased wool was divided into six half-pound lots. These samples were placed in clean muslin bags. One bag was submerged in two pounds (935 cc.) of warm water in a jar and agitated by hand for two minutes. The bag was then removed, squeezed as dry as possible, and placed in a second jar containing 935 cc. of warm water (45° C.). After agitating for two minutes, the bag was removed, squeezed, and placed in a third jar, and so on through eight jars. The solution removed from the jars by the sample was replaced in each jar by enough liquor from the succeeding jar (counter current system), the last

jar being replenished with clean warm water. The other lots were then put through the same treatment as the first and so on until the six half-pound lots had passed through the solutions, which were then analyzed with the results shown in Table 9.

TABLE 9

COMPOSITION OF LIQUORS FROM DEGREASED WOOL

Jar No.	Total Solids	Soluble Solids	Grease	Soluble Potash (K_2O)	Nitrogen
	%	%	%	%	%
1.....	22.9	9.7	1.3	3.5	0.8
2.....	14.7	8.1	0.9	2.6	0.6
3.....	8.6	6.6	0.5	1.4	0.4
4.....	4.4	2.3	0.3	0.6	0.2
5.....	2.5	1.2	0.2	0.4	0.1
6.....	1.5	0.6	0.1	0.2	0.07
7.....	0.8	0.4	0.0	0.1	0.04
8.....	0.5	0.2	0.0	0.1	0.03

The volume and specific gravity of the liquid in each jar was as follows: No. 1, 500 cc., 1.047; No. 2, 920 cc., 1.059; No. 3, 1020 cc., 1.027; No. 4, 910 cc., 1.010; No. 5, 910 cc., 1.001; No. 6, 1020 cc., 0.98; No. 7, 930 cc., 0.95; No. 8, 980 cc., 0.93.

The liquors in jars 1 and 2 were rather thick and heavy, owing largely to the tendency of the albuminous matter to thicken slowly, even at 45° C., and to the presence of a large quantity of sand and dirt, approximately 12 per cent in jar 1 and 6 per cent in jar 2. These liquors remained sufficiently fluid for washing the wool during the hour that was required to conduct the experimental washings at 45° C., but set to a jelly on cooling over night. It is doubtful, therefore, whether sedimentation of the liquor from the first bowl would be sufficiently rapid to materially reduce the proportion of suspended matter carried by liquor of this concentration. It seems probable, however, that if the liquor flowing from the second bowl to the first were passed through a centrifuge and the liquor withdrawn from the bottom of the front end of the first bowl, passed through a second centrifuge, and returned to the back end, a large part of the suspended matter could be removed, thus decreasing the cost of further concentration. However, experimentation on a large scale will be necessary to determine the feasibility of doing this.

The concentration of the liquor in the fourth jar is about the

same as that of the ordinary soap and water "scour" in the first bowl (except, of course, in grease), and that of the liquor in the eighth jar approximates that of the liquor in the fourth bowl of the ordinary scouring liquors.

The results thus obtained plainly show that it is possible to obtain a higher concentration of potash by using degreased wool; that more of such wool can be scoured in the same volume of water than when using raw wool, and although the potash concentration was not as high as expected, this concentration (3.5 per cent) could be treated, it is believed, on a commercial scale for the recovery of potash at a profit.

Fertilizer Materials from Waste Liquors

While the experimental work here outlined was in progress, experiments on working the waste into fertilizers were being conducted.

Sample No. 1, the concentrated waste liquor from New England, containing 60 per cent solids, 14.4 per cent potash, and 1.2 per cent nitrogen, was mixed with several phosphatic materials in several proportions, dried, and run through a small mill. Sample No. 2, made with 83 per cent acid phosphate and 17 per cent concentrated waste liquor, contains 0.3 per cent nitrogen, 15½ per cent phosphoric acid, and 2.2 per cent potash. Sample No. 3, made with 68 per cent acid phosphate and 32 per cent concentrated waste liquor, contains ½ per cent N, 14 per cent phosphoric acid, and 4.1 per cent potash. Sample No. 4, made with 46 per cent acid phosphate, 37 per cent raw bone meal, and 17 per cent concentrated waste liquor, contains 1.8 per cent N, 21 per cent phosphoric acid, and 2.3 per cent potash.

Two factory-scale tests were also run. In the first, in cooperation with J. C. Cottman & Co., Baltimore, Md., 12 barrels (600 gallons weighing about 5,500 pounds) of the concentrated waste liquor was mixed with approximately the same weight (dry basis) of raw scrap leather. The mixture was steamed, dried and ground. Sample No. 3, which contains 6.1 per cent nitrogen and 6½ per cent potash, is representative of this product. In cooperation with the Standard Guano Co., Baltimore, Md., 100 barrels of the concentrated waste liquors were used in making a complete fertilizer for which the mixing formula was 810 pounds 54° acid, 800 pounds ground phosphate rock, 550 pounds hair and wool waste, and ¾

barrel concentrated waste liquor. When the "den" was opened, 10 barrels of dark thin grease were collected. Sample No. 6 was taken from this material, which contains 0.95 per cent nitrogen, 15.17 per cent available phosphoric acid, 0.9 per cent potash, and 1 per cent grease. This in our experiments showed good results in growing wheat, corn, and cowpeas on soil of three widely different types.

Both of the factory scale experiments conducted to determine the practicability of working up the concentrated waste liquor proved entirely feasible and economical. The primary question with the fertilizer manufacturers is whether the material can be had in sufficient quantity and at a price per unit of nitrogen and of potash that will compare favorably with the prices of other raw materials. It is, of course, perfectly obvious that the initiative must come from the scourers. They must furnish the material in quantities and at a price that will prove attractive to fertilizer manufacturers. We believe this is possible.

Value of Recoverable By-Products

It has been said that "Figures do not lie, but liars figure." By using high values and a good measure of optimism, large profits may often be shown upon paper—but never realized. We want to avoid such an outcome. We prefer to paint the picture darker than we believe it actually is.

From the average analytical figures obtained in examining the 300 samples of raw wool (slightly reduced) and the minimum market price of the several important constituents, it is practicable to obtain what we believe are reliable approximate gross values for the by-products from any given quality of wool.

The estimated approximate value of wool waste by-products based on 100,000 pounds of wool is as follows:

Neutral grease (10 per cent),	10,000	pounds at	7¢ lb.	$700.00
Potash (K_2O) ($3\frac{1}{2}$ per cent),	3,500	" "	3¢ lb.[2]	105.00
Nitrogen ($1\frac{1}{2}$ per cent),	500	" "	15¢ lb.[3]	75.00
Filler (sand and dirt) (15 per cent),	15,000	" "	0.1¢ lb.	15.00
Total (29,000 pounds)				$895.00

That is, a low estimate of the yields from 100,000 pounds of average raw wool is approximately 10,000 pounds of neutral grease, worth

[2] Basis of kainit price.

[3] Basis of garbage tankage price.

about $700, and 19,000 pounds of fertilizer material, worth about $195, giving a total gross value of about $895.

Practicability of Waste Recovery and Utilization

This briefly covers our study of the problem. Our funds were exhausted at this stage where small industrial scale work is necessary in order to definitely answer the question "Can waste wool-scouring liquors be economically recovered?" Like others who have studied the subject, we can not answer the question categorically. Our firm belief, based on a careful consideration of the work of others and on our own experiments, is that it can be done. Perhaps it will be done at a considerable profit. Let us hope so. Perhaps it will be done at a return that barely covers the cost. Even so, it is well worth the doing for sanitary and industrial reasons alone, and the present is as good a time as any to begin.

It should be undertaken and financed cooperatively by a group of wool scourers, at one of the scouring mills, utilizing the experience which has been acquired during the past ten years.

It is going to require patience, courage, ability, and money. If it were an easy problem, it would have been solved years ago. It may take one year and cost $25,000 or it may take five years and cost $200,000. It's worth it.

It is going to require modifications in present scouring machinery and perhaps profound changes in scouring processes. Here is where patience and courage are required, but there seems to be plenty of room for improvement.

If such a group, such funds, and such cooperation can be had, the Bureau of Chemistry will be glad to lend its earnest aid in solving the problems of the recovery and utilization of wool-scouring waste, in a united endeavor to improve sanitary and industrial conditions and to increase the fertilizer resources of the country.

Discussion

Mr. Martin L. Griffin: The subject is a very old one from various angles. If you will consult the patent literature of 35 or 40 years ago you will find that extracting processes were exploited at that time. I was, myself, interested in this work some years ago here in Providence. A machine was sold here with the intention that by simple evaporation they could produce wool grease from the suds. There was a good deal of prejudice at that time against the

extraction process of wool, but I believe it is possible to remove the grease at its source, and that it is perfectly impossible to properly condition the wool so that an equally good product can be made thereafter.

PROF. LOUIS A. OLNEY: Unfortunately I was not here at the very beginning of this paper. The subject is one in which I am very much interested. I believe the facts are true as presented in regard to the possibilities of recovering wool grease and potash compounds in this country. But on the other hand I believe that a number of manufacturers who produce large quantities of wool scouring waste liquors have tried out at different times the recovery of these compounds and they eventually gave it up, because it was not a profitable venture. Nevertheless, there are cases where they have to recover, or have to purify the waste liquor before it goes into a stream on account of legal requirements and under these circumstances they have often times carried out processes quite exhaustively, and I believe that in these instances they feel quite well satisfied with the results if they get back a new dollar for an old one. In many instances the process has been carried on at a loss, so that the experience of the textile industry is such that it is rather difficult to get the textile manufacturers to go into any expensive recovery process.

I presume many of you are acquainted with the fact that the Arlington Mills at Lawrence, for some 30 years have recovered wool grease by the naptha extraction process very successfully, and at times profitably. That is the ideal way of recovering wool grease, but the initial expenditure for a satisfactory and safe plant is prohibitive in most cases.

A plant suitable for extracting wool grease by the naphtha process satisfactorily would require almost as much capital, I was going to say, as the woolen mill for which it recovers the grease and it is only on a very large scale that it can be done satisfactorily or economically. But as time goes on the subject will be studied more from the point of economical procedure and we will then find that wool grease can be recovered more satisfactorily and also more of the potash salts may be recovered if the market will permit. One of the great difficulties has been in the past to produce wool grease and potash salts cheap enough to compete with foreign products and also home competition has sometimes been an unsettling factor.

Mr. Stuart E. Coburn: There is a plant on the Neponset River, one of the largest wool scouring plants in Massachusetts, where the wool men were opposed to the solvent process due to its making the wool harsh. At present they are using the acid cracking process for the recovery of wool grease from the scouring liquors. During the war period, they used the centrifugal method. At that time wool grease was bringing about 25 cents a pound and the centrifugal method was successful from a financial view point, although they recovered only about 50 per cent of the grease. At present the acid cracking process, which removes 90 per cent, is being used. This process costs 5 cents per pound of grease while the value of the grease is about 3½ cents, so that the net loss is about 1½ cents a pound for every pound of grease that is produced. But they do it for the health side of the question and also the purity of the river.

Dr. James R. Withrow: I would like to ask in this last case whether it is possible to dispose of the acid wastes in this way?

Mr. Coburn: No, because the acid wastes go into the other alkaline wastes and are neutralized in that way. We are attempting to hold the final quantity of the effluent after treatment to 5.4 pH. In many places it runs way above that, which is not necessary.

Mr. E. B. Besselievre: Mr. Benedict in his paper brought out the possibilities in recovery of the grease but did not cover the question of the treatment of the effluent to prevent or eliminate stream pollution. That is the most difficult problem that we find; you can get the grease out but you still have the waste in a very bad condition.

Mr. Benedict: We had just reached that point and intended to take it up with the industries when our appropriation lapsed and we had to drop it. We intended to work it out on a practical industrial scale but had to stop the work.

Mr. Besselievre: Then you intend to go on with the work?

Mr. Benedict: Yes.

Dr. Hugh K. Moore: I desire to speak of one thing, about the pollution of streams, which has not been brought out, and that is that some pollution of streams is done unintentionally. For instance, where streams are used in the case of railroads for the transportation of logs, the amount of soluble matter arising from the presence of the logs in the stream, is enormous. If you are making a pulp that you are bleaching, the consumption of bleaching liquor

due to the soluble matter from these logs in the stream is really of considerable importance. At Berlin (N. H.) we are at the head of the stream, and there is nothing ahead of us so far as plants are concerned, but the consumption of bleaching liquor due to the organic matter from the logs, is considerable, and the only way to get rid of it and make economies is to use less water. So that we are now doing our bleaching in a run of between 20 and 25 per cent of stock in our bleacheries, in order to get rid of this immense consumption of bleach due to the soluble matter coming down the river. I do not see any solution for that, because there are no railroads and practically all the material has to come down the river.

Mr. M. L. Griffin. At Rumford, Maine, further down the stream, we were confronted with that trouble, and the extra pollution caused by Mr. Moore's company, the Brown Company.

Prof. A. H. White: I would like to ask some of these gentlemen about the future. I have understood that the states were becoming more rigid in their laws, and that probably the time was not far away when nearly all manufacturing industries would be required to purify the streams that traverse settled country, so that the problem is one which will become more and more important as time goes on. We have heard of the allocation of streams in Canada. Is there much of that in this country, and is it likely that firms can locate on a stream passing through industrial communities and have any certainty that they will be allowed to continue to pollute that stream, except within very narrow limits?

Mr. E. B. Besselievre: That subject of the state's relation to industry, Professor White, will be heard on Friday morning, the first paper being by Mr. W. L. Stevenson of Pennsylvania who will cover that point. The State of Pennsylvania has looked at the problem from that viewpoint, i.e., fairness to the manufacturer and looking to the future protection of public health and the paper of Mr. Stevenson will outline the way they have worked it out in Pennsylvania. I do not know that any other states have gone into the problem as definitely or completely, but I believe that Ohio is patterning a new law after the Pennsylvania law. Mr. Gage may know of that.

Mr. Stephen DeM. Gage: Many states are considering that proposition. In Rhode Island the Board of Purification of Waters was created to clean up our streams and tidal waters. Under the law this Board has full authority to stop pollution wherever it may

be found. To order pollution stopped immediately, however, would mean in many cases that important industrial plants would have to close down until proper purification plants could be installed. In the exercise of its authority therefore the Board must use a large amount of discretion and take into consideration the effect which any order to stop pollution would have on the industrial life of the state. The policy of the Board has been to bring the necessity of cleaning up the streams to the attention of the manufacturers who are causing pollution and to ask their cooperation in reducing that pollution to the minimum. The manufacturers have all shown a hearty spirit of cooperation and everybody is working together for the best interests of all parties concerned in the problem.

At the present time neither the Board of Purification of Waters nor any other Board has any authority towards conservation of our streams and other inland waters. The fact that the continued growth of our municipalities and our manufacturing industries depends in a large mesaure upon the conservation and proper allotment of the water resources of the state is beginning to be recognized. At the last Legislature a bill was presented to create a conservation commission to study the water resources of the entire state in respect to the needs of municipalities and industries and also in respect to the necessary use of the streams as the ultimate disposal of sewage and manufacturing wastes. While this bill failed of passage agitation in favor of some legislation of this character is growing.

Dr. James R. Withrow: In connection with the Ohio situation the Legislature has recently passed a law. There has been increased pressure on the Legislature for amelioration of the conditions in the streams, and to some of us it appears that the pressure has been quite unreasonable.

The member of the Governor's cabinet, in charge of the State Department of Health, has taken the position that he should not take any steps which were not taken in consultation with the manufacturers, and most of us have felt that that was the right procedure.

A similar pollution matter comes up frequently in connection with the deadly carbon monoxide from gas fumes. We found to our sorrow in Ohio that although manufacturers of stoves were apparently in favor of prevention of the high death rate, yet they were able to bring pressure upon the gas companies in the eastern

part of the United States to send a large lobby into our Legislature to prevent relieving the conditions. We have a known death rate of 52/100 from carbon monoxide, due to poorly constructed stoves, in a population of 7,000,000.

In the case of the stream pollution this year it was quite a different matter. At a meeting this year the Ohio State Department of Health got in touch with the men in the state who were responsible for the pollution from paper mills which exists. The State Board of Health has a very definite program for cleaning up the streams and the manufacturers discussed it with them frankly and fairly, and the net result has been cooperative effort which looks as if it would result in great satisfaction to all concerned. It looks as if it would be a satisfactory solution. The Health officials and public opinion are putting on the pressure harder and harder all the time, in the matter of prevention of stream pollution. There can be no question about that.

Mr. W. D. Collins: The Geological Survey receives many requests for information regarding localities where waters of certain characteristics can be found in the United States. Chambers of Commerce and other trade bodies ask for analyses which they can use to induce people to locate their plants where these good waters are. There appears to be little effort to prevent future trouble in regions where manufacturing is not now carried on extensively.

The tendency seems to be for the Chambers of Commerce to try to get a factory located in a neighborhood regardless of whether that factory will keep out a dozen others. If the states where no large manufacturing now exists could be induced in some way to take hold of the matter earlier, and prevent some of these troubles that come when pollution has to be regulated after the factories are running, they could give the assurance that Professor McKee was asking for—that if a company is permitted to pollute a river they will always be permitted to pollute it, or that when locating they will know how much purification will be required. Perhaps manufacturers ought to consider more carefully than they have, the question of future conditions, instead of merely hunting a place where now the water is good.

Dr. Henry Howard: It seems to me that while that would be very desirable from a manufacturer's point of view, it is practically impossible, because no legislative body can pass any laws which will bind its successors, and while one Legislature may agree with a

certain manufacturer that he may pollute a stream indefinitely, another Legislature 25 years hence may pass an entirely different law, and even if the state legislature does not change it the Federal Government may step in if the stream goes down in to some other state and affects adversely the manufacturers there. I do not see therefore, how such a scheme can ever be worked out.

Dr. John C. Olsen: One of our difficulties is that we have various states and various policies and a manufacturer of woolen goods in one state might be compelled to purify the effluent, and thereby be handicapped in competition with manufacturers in other states who would not be so required to purify. Will it not result in having federal legislation as Mr. Howard suggests, so that conditions will be uniform? If our plants are put under the necessity of purifying the effluent, they will be able to compete and not be under the difficulty of unfair competition. To get all the states to cooperate and pass a uniform law would be very difficult, and I wonder if this is not a case where we will centralize as we have been doing in the past few years, so that conditions can be uniform in this respect?

Dr. Ralph H. McKee: It has just been mentioned that a lobby entered into the question by opposing certain regulations. I do not think that we appreciate as much as we should the probabilities of very strong lobbies taking a hand in the near future, in connection with the purification of streams. I am referring particularly to the Isaac Walton League, and the Merchants Association of New York State. Both of those organizations have already passed resolutions and very troublesome resolutions, for certain types of manufacturing plants. If these regulations later become laws they will give us as chemical engineers a great deal of work to do.

F. B. Besselievre: We find, Professor McKee, that particularly in Pennsylvania has that been true lately. The present Governor Mr. Pinchot is a great sportsman, and lives in a fishing country. All the fishermen up there have gone to the Governor, asking him to get a law to prevent the pollution of streams by the tanneries which have been polluting there for years. The state got active and a joint committee was selected by the state and the Tanners Council, to experiment for a number of years and find the most economical system of treatment to guide the State in ordering the construction of Treatment Plants. That shows what lobbies can do.

As to the other question, of getting together, New York State, Pennsylvania and New Jersey have appointed a joint committee to have control over the Delaware River, especially to determine the degree of the treatment which shall be used at various points on that river, mainly for sewage to be sure, but it results in scientific consideration and progressive treatment on that river all the way up.

Mr. Hadley: We have a fish box containing 50 to 100 fish where they get the output of our strong effluent, the output before any of it reaches the river and they appear to thrive on it.

Dr. Olsen: What kind of waste product is that?

Mr. Hadley: Dye house and mercerizing plant.

Dr. Olsen: And the fish like it, do they?

Mr. Hadley: They are what we call Kelleys down in New Jersey.

Mr. Besselievre: Mr. Hadley, you gave the impression or at least Dr. Olsen did that the fish lived in the unpurified waste.

Mr. Hadley: Oh, no, in the effluent, after it was ready to go into the river.

Dr. Hugh K. Moore: We have done a lot of work in training certain bacteria, and they get acclimated so that they thrive in sulphite liquor waste. We have a graduated method. We make a more or less nutritious food and add a few drops of the effluent. And then later on a little more, so that after a year or so we can put them into 25 per cent concentrated sulphite liquor and that ferments and goes on developing. But you have to acclimate them gradually. That might be done with fish.

Prof. James R. Withrow: We are interested in these problems of waste disposal and stream purification. We must admit there are annoying difficulties. Nevertheless, we must not forget that very successful work has been done in many cases. I have just come from a very large Merrill-Soule powdered milk plant where they have had a great deal of trouble in the past, with the effluent from washing milk cans and so on. Now they have a beautiful little plant for taking care of their problem. It occupies a space not longer than half of this room, and contains three concrete tanks. One workman takes care of the whole of the work and the water flows continuously into one or another of the tanks. He puts in a little sulphate of iron as he starts filling the tank, and later a little hydrated lime. The tank is aerated and allowed to settle. In 30 to 60 minutes the tank has settled and is decanted to the stream.

The mud goes upstairs and stands awhile, the tank is decanted and then the mud is taken out and dumped on the soil. It shows how simply one man with a simple cheap plant can handle the situation.

As the problem becomes more difficult it requires a great deal more attention. But many of these problems are solved in a very simple manner.

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